Air Quality Related Values and Development of Associated Protocols for Evaluation of the Effects of Atmospheric Deposition on Aquatic and Terrestrial Resources on Forest Service Lands

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Executive Summary

The USDA Forest Service collects and analyzes data on natural resource sensitivity and the effects of air pollution on aquatic and terrestrial ecosystems throughout the national forests nationwide. Such studies are often conducted at the individual forest level. At the present time, there are no standard protocols to guide field sampling, laboratory analysis, or data analysis associated with such activities.

There is broad agreement that the air quality related values (AQRVs) on Forest Service lands that are sensitive to potential degradation from atmospheric deposition of sulfur (S), nitrogen (N), or toxic substances include surface water and associated aquatic biota, soil, and flora. There is much less agreement, however, regarding what are the most important sensitive receptors of these AQRVs, or what should be used as indicators to document the occurrence of an adverse impact on a sensitive receptor.

This report summarizes the results of a scoping study to evaluate AQRVs and associated existing field, laboratory, and data analysis protocols to be used in characterizing the health and status of components of aquatic and terrestrial ecosystems that are affected by atmospheric deposition of S, N, and toxics. The objective is to provide the foundation for developing a standard set of Forest Service AQRVs, sensitive receptors, indicators, and associated protocols to guide field studies on AQRVs nationwide.

Both chemical and biological sensitive receptors are assessed. Emphasis is placed primarily on acidification and eutrophication effects associated with deposition of S and N, and secondarily on effects associated with Hg, pesticides, and other toxic materials. The AQRV protocol development work is intended to occur in two phases. During Phase I, which is the subject of this report, we focus mostly on indicator selection, and the ways in which indicators can or cannot be used for assessment purposes. We also provide a summary of a number of existing protocol documents which may be helpful in refining the Forest Service AQRV program.

Where appropriate, standard national protocols should be considered for possible adoption by the Air Program for collecting, processing, and interpreting data regarding the effects of atmospheric deposition on natural resources on Forest Service lands. The use of standardized protocols would foster consistency across individual forests and maximize the Agency's ability to assess spatial and temporal trends in resource sensitivity and environmental effects. Use of consistent approaches in the collection and interpretation of environmental data

would help efforts to understand cause/effect relationships among air pollution, biogeochemistry, natural resource sensitivity, and land management.

A variety of air pollutants have the potential to stress aquatic and terrestrial ecosystems. Both the pollutants and the types of potential effects are variable. For this report, we focus mostly on atmospheric pollutants that contribute to soil and/or water acidification and eutrophication (nutrient enrichment). Both atmospheric S and N have the potential to cause acidification. Atmospheric N can also cause eutrophication where N supply is limiting. We also address, with lesser coverage, the effects on biological resources of atmospheric contributions of Hg and other toxic materials.

Large areas throughout the United States contain substantial populations of lakes and streams having low acid neutralizing capacity (ANC). These include much of the Northeast, mid-Appalachian Mountains, southern Appalachian Mountains, northern Florida, Upper Midwest, and the western United States. The eastern states include many acidified surface waters that have been impacted by acidic deposition. The western states contain many of the surface waters most susceptible to potential acidification effects, but the levels of acidic deposition in the West are generally low and acidic surface waters are rare. Many of the areas having acid-sensitive surface waters, especially in the northeastern United States and Appalachian Mountains, also contain extensive areas with acid-sensitive soils.

Nitrate (and also ammonium [NH_4^+] which can be converted to NO_3^- within the watershed) has the potential to acidify soils, soil waters, and surface waters. However, N is a limiting nutrient for plant and microbial growth in most terrestrial, and some aquatic, ecosystems. Therefore, atmospheric N deposition has the potential to contribute to increased productivity, eutrophication, and N-saturation in remote locations. Forest soils usually leach relatively little NO_3^- into surface waters. For that reason, increased atmospheric deposition of N does not necessarily cause adverse aquatic environmental impacts. In many areas, added N is taken up by terrestrial biota and the most visible effects include an increase in forest productivity and competitive shifts among plant species based on their N requirements. However, in some areas, especially at high-elevation sites, terrestrial ecosystems have become N-saturated and high levels of deposition cause elevated levels of NO_3^- in drainage waters. Enhanced leaching of NO_3^- in response to N-saturation can cause depletion of base cations from forest soils, adverse impacts on sensitive tree species, and acidification of drainage waters in base-poor soils.

Mercury (Hg) is naturally occurring and is found throughout the environment. Mercury present in fossil fuels is released to the atmosphere during combustion, and is subsequently available for long-range atmospheric transport and deposition to the earth surface. It enters lakes and rivers from atmospheric deposition of the Hg emitted by air pollution sources and also from nonpoint sources via erosion and runoff.

Mercury is a toxin that can damage the human brain and nervous system. The developing fetus and young children are particularly susceptible to the toxic effects of Hg. Human exposure to Hg mostly occurs via consumption of fish and other seafood that has accumulated high concentrations of Hg. Fish consumption advisories for various lakes and rivers have been issued in most states throughout the U.S.

Pesticides applied to agricultural crops can become volatized or suspended in the atmosphere with dust particles, and eventually be transported with prevailing winds to remote areas. There are a variety of other toxic chemicals that can be atmospherically deposited, some of which have the potential to bioaccumulate. These include polychlorinated biphenyls (PCBs) and some fire retardant chemicals.

Atmospheric inputs of both S and N can cause acidification of soil, soil water, and fresh drainage water (lakes, streams). In most regions of the United States that have experienced acidification impacts from air pollution, those impacts have mainly been due to S deposition. There are also, however, some regions, especially in the western U.S., where resources are more threatened by N inputs than by S inputs. This is at least partially due to the very low levels of S deposition received at many western locations. There are also regions (portions of the Northeast, West Virginia, high elevations in North Carolina and Tennessee) where both atmospheric S and N contribute substantially to the observed acidification.

Eutrophication, or nutrient enrichment, is a potential consequence of N deposition to both aquatic and terrestrial ecosystems. Many freshwater ecosystems are phosphorus (P)-limited, and therefore would not be expected to increase primary productivity in response to increased atmospheric inputs of N. However, there are examples of fresh waters which appear to be N-limited or N and P co-limited. They mostly occur in remote locations at relatively high elevation, especially in the western United States. In such aquatic systems, atmospheric inputs of N would be expected to increase productivity and/or alter biological communities such as phytoplankton.

Atmospheric deposition can contribute to toxicity responses in several ways. The atmospheric pollutants of concern with respect to toxicity are primarily Hg and pesticides. Atmospheric deposition is an important component of Hg cycling and biogeochemistry. Mercury is known to bioaccumulate in aquatic organisms, reaching potentially high concentrations in larger, piscivorous fish.

There are three ecological AQRVs on Forest Service land that are susceptible to air quality degradation: surface water, soil, and flora. There are a variety of potentially important sensitive receptors for each AQRV. Sensitive receptors for effects on surface water could include water chemistry, productivity, and the response of important life forms, including fish, zooplankton, benthic macroinvertebrates, and phytoplankton. Key sensitive receptors for assessing impacts on soil include soil chemistry and soil solution chemistry. Sensitive receptors for flora include macro-lichens and acid-sensitive vascular plant species. In particular, evidence has accumulated that suggests adverse impacts from acidic deposition on red spruce and sugar maple at some locations in the eastern United States. The picture is less clear for effects of deposition on western trees, although some common western tree species (mainly ponderosa and Jeffrey pine) are known to be sensitive to O_3 damage.

High leaching of NO_3^- in soil water and streamwater draining high-elevation spruce-fir forests has been documented in numerous studies in the Southern Appalachian Mountain (SA) region. This high NO_3^- leaching has been attributed to a combination of high N deposition, low N uptake by forest vegetation, and inherently high N release from soils.

Epiphytic macro lichens (those that grow attached to trees or other plants) are generally good indicators of air pollution. Their tissue content of contaminants is generally reflective of the amount of ambient atmospheric pollution. Individual species exhibit different sensitivities to atmospheric pollutants, with some species being adversely impacted at air pollution levels that may not be considered high relative to other AQRVs. Assessment of long-term change in the epiphytic lichen community can be especially valuable to provide an early indication of either improving or deteriorating air quality and atmospheric deposition. Such monitoring was incorporated in 1994 into the U.S. Forest Service Forest Inventory and Analysis (FIA) Program.

Concerns have been cited since the early 1970s about potential forest declines that could result from soil acidification and nutrient deficiency brought about by acidic deposition. In addition, concerns have arisen regarding the mobilization of aluminum (Al) in forest soils due to inputs of acidic deposition, and the potential toxicity of that Al to forest stands.

Acidic deposition has contributed to a decline in the availability of Ca^{2+} and other base cations in the soils of acid-sensitive forest ecosystems by the leaching of base cations from foliage and from the primary rooting zone and by the mobilization of Al from soils to soil solution and drainage water. Both N and S deposition have contributed to these mechanisms. Foliar Ca^{2+} levels and soil and root Ca:Al ratios are considered low to deficient over large portions of the spruce-fir region in the eastern United States. Aluminum mobilization from already acid soils can also impede Ca^{2+} and magnesium (Mg^{2+}) uptake and potentially induce plant deficiencies in these nutrients.

The weight of evidence for spruce trees suggests that adverse impacts on soil solution chemistry are likely, and adverse impacts on forest growth and health are possible. Changes in red spruce growth rates are potentially attributable, at least in part, to base cation deficiencies caused by inhibition of base cation uptake by trees due to elevated Al concentration in soil solution within the rooting zone. Other factors that could also be important include depletion of base cations in upper soil horizons by acidic deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidic deposition, especially cloud deposition.

Forest trees are not the only vascular plants that are potentially sensitive to acidic deposition. Available data suggest that some tree species can be sensitive to base cation depletion and/or Al toxicity, and it is possible, or perhaps likely, that a variety of shrubs and herbaceous species are similarly sensitive. Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in response to acidic deposition. Data are insufficient in this country, however, to allow us to use shrub or herbaceous plant species as indicators of the effects of acidic deposition at this time.

The possible effects of acidic deposition on wetland, riparian, meadow, and alpine plant communities are also of significant concern. Especially important in this regard is the role of N deposition in regulating ecosystem N supply and plant species composition. Key concerns are for listed threatened or endangered species and species diversity. However, for most rare, threatened, or endangered herbaceous plant species, little is known about their relative sensitivities to atmospheric deposition inputs. Although species diversity is highly valued, it can be difficult and expensive to document changes in this parameter in response to atmospheric deposition.

Forest health is an elusive concept. It can be reflected by a variety of physiological indicators, including, for example, changes in the growth rate of trees, foliar damage, susceptibility to insects or disease, and tree mortality. Similarly, forest health can be affected by a host of potential stressors, of which air pollution is only one possibility. Climate, stand competition, outbreak of non-native pathogens, and forest management (alone or in combination) often contribute greatly to observed forest health problems. Attempts to document, and in particular to quantify, the effects of air pollution on forest health have encountered considerable complexity and uncertainty. Nevertheless, such efforts have produced some evidence that suggests that red spruce, and perhaps also sugar maple, in some areas have experienced declining health as a consequence of acidic deposition.

It is important to note that, at most forested locations in the United States, it is unlikely that terrestrial effects of atmospheric deposition can be documented by conducting vegetation studies. This is because levels of atmospheric deposition of S and N are usually below expected damage thresholds for most tree species, assessment of forest health is extremely complex, and trees typically respond to a wide variety of stressors in addition to atmospheric deposition. It is therefore more likely that the results of vegetative studies will be useful as corroborating evidence, to be used in conjunction with results of analysis of soil and/or drainage water chemistry when assessing AQRVs.

When vegetation analyses are conducted as part of Air Program studies, it might be helpful to use protocols that are already in place within existing Forest Service inventory and monitoring programs. Forest Inventory Analysis field methods for vegetation diversity and structure were derived from the Forest Health Monitoring Program.

There are many approaches that can be used by the Forest Service to assess 1) the sensitivity of aquatic and terrestrial natural resources to potential degradation from atmospheric deposition of S, N, or toxic materials, and 2) the extent to which sensitive aquatic or terrestrial natural resources have been harmed in the past or might be expected to be harmed in the future under assumed scenarios of air pollution and atmospheric deposition. We highlight a number of approaches that can be broadly useful to the Forest Service across the United States. We recommend that such approaches be routinely considered in making evaluations regarding atmospheric deposition sensitivity and/or effects. A number of existing protocol reports are summarized.

AQRVs are resource elements that could be damaged by air pollution or atmospheric deposition. They include water, flora, soil, cultural resources, geological features, and visibility. For this report, we focus only on measurements of sensitive receptors for the first three of those types of AQRVs. There are many possible sensitive indicators for each AQRV. For example, to protect the AQRV lakewater, sensitive receptors might include the chemistry of the water, which could influence its suitability to support various aquatic species and life forms. There are also sensitive biological indicators, which reflect the suitability of the lakewater for supporting aquatic organisms which might be sensitive to acidification or eutrophication. These could include, for example, fish, zooplankton, or diatoms. A sensitive receptor can be evaluated by taking measurements of indicators of injury or ecosystem change. For example, ANC is an indicator of change in the sensitive indicator water chemistry.

A limited list of key variables does not exist with which to measure ecosystem condition, or ecosystem response to stressors, such as those associated with atmospheric deposition (i.e., acidification, eutrophication, toxicity). Ecosystems are highly complex, and simply cannot be represented by a handful of variables. Nevertheless, there are variables that have been shown to be, or that are expected to be (based on existing research), reflective of the general level of ecosystem harm that might be associated with atmospheric deposition. We propose a set of consistent AQRVs and associated sensitive receptors that could be used by the Forest Service nationwide for evaluation of ecosystem sensitivity to, and effects from, atmospheric deposition (Table ES-1). Individual forests may wish to augment, or replace, some of the listed items in favor of other AQRV receptors that are especially important to a particular forest region or location, or for which that forest has specialized expertise. Nevertheless, the recommended AQRVs and sensitive receptors summarized here are broadly applicable and reflect a range of aquatic and terrestrial effects of atmospheric deposition. These receptors and indicators will help determine the protocols that will be needed by the Air Program for nationwide research and monitoring.

Detailed protocols should be an important part of any resource characterization and/or monitoring program intended to evaluate atmospheric deposition impacts on AQRVs. Protocols will help to ensure that measured differences among locations or changes over time at one location actually occur in nature, and are not simply a reflection of different methods, sampling personnel, or timing of sample collection. Protocols are necessary to ensure data quality

and credibility, and to allow determination of temporal trends or spatial patterns in resource sensitivity or level of effect.

Table ES-1. Straw-person recommended AQRVs, sensitive receptors, and indicators affected by atmospheric deposition of air pollutants for application to Forest Service lands nationwide.

AQRV	Sensitive Receptor	Indicator/Metric	Potential Criteria*
Flora	red spruce (East)	growth decline	change in diameter change in extent of damage
	sugar maple (East)	growth decline	change in diameter change in extent of damage
	lichens	community composition	loss of sensitive taxa
Soil	soil chemistry	base saturation exchangeable Ca^{2+} exchangeable $Ca^{2+} + Mg^{2+}$ C:N molar ratio	BS < 10% % change over time % change over time C:N < 0.2
	soil solution chemistry	Ca:Al molar ratio $[Ca^{2+} + Mg^{2+} + K^{+}]$:Al molar ratio NO_3^- concentration	Ca:Al < 1.0 BC:Al < 1.0 $NO_3^- > 20$ μeq/L during growing season
Surface water	water chemistry	acid neutralizing capacity NO_3^- concentration SO_4^{2-} concentration	ANC < 50 μeq/L $NO_3 > 10$ μeq/L change over time
	water productivity	chlorophyll *a* clarity (lakes)	change over time change over time
	fish	salmonid species presence fish species richness fish condition factor fish Hg concentration fish pesticides(s) concentration	loss over time change over time change over time Hg > 0.3 ppm above threshold values
	zooplankton (lakes)	total zooplankton richness crustacean taxonomic richness rotifer taxonomic richness	change over time change over time change over time
	benthic macroinvertebrates (streams)	mayfly taxonomic richness Index of Biotic Integrity	loss of sensitive taxa deviation from reference
	diatoms	community composition	historical change from paleolimnological reconstruction

* Metrics can be represented in multiple ways, often as change over time detected in a monitoring program or as exceedence above or below a threshold value. Typically, multiple threshold values are possible. For example, surface water target ANC thresholds are commonly set at 0, 20, or 50 μeq/L to achieve different levels of protection.

1. INTRODUCTION

The USDA Forest Service collects and analyzes data on natural resource sensitivity and the effects of air pollution on aquatic and terrestrial ecosystems throughout the national forests nationwide. Such studies are often conducted at the individual forest level. At the present time, there are no standard protocols to guide field sampling, laboratory analysis, or data analysis associated with such activities. A number of protocol documents have been written by the Forest Service and other agencies to address various aspects of air pollution effects studies. None, however, brings together all of the elements needed to standardize Forest Service approaches to gathering, analyzing, and interpreting field data.

There seems to be broad agreement that the air quality related values (AQRVs) on Forest Service lands that are sensitive to potential degradation from atmospheric deposition of sulfur (S), nitrogen (N), or toxic substances include surface water, soil, and flora. There is much less agreement, however, regarding what are the most important sensitive receptors of these AQRVs, or what should be used as indicators to document an adverse impact on a sensitive receptor. In some cases, however, the selection is rather unambiguous. For example, it is universally accepted that acid neutralizing capacity (ANC) is a good indicator of effect on an important sensitive receptor (water chemistry) of the AQRV surface water. Nevertheless, there is less certainty regarding what should be considered to be a critical cutoff value for adverse biological effects associated with declining surface water ANC. This is partly due to the fact that different aquatic species, and different life stages of a given species, exhibit varying degrees of sensitivity to change in ANC. Some aquatic biota are affected at ANC near zero, whereas others are affected if ANC falls below a cutoff near 50 μeq/L, or even higher. Furthermore, it is not necessarily clear how or when a particular indicator should be measured. Again, using the example of surface water ANC, there are multiple ways to measure ANC, using laboratory titration procedures or ion balance calculations. In addition, ANC varies in a lake or stream with season and with changes in hydrological conditions. ANC during a rainstorm or snowmelt event may in some cases be 20% or more below the ANC value measured during low flow conditions.

This report summarizes the results of a scoping study to evaluate AQRVs and associated existing field, laboratory, and data analysis protocols to be used in characterizing the health and status of components of aquatic and terrestrial ecosystems that are affected by atmospheric deposition of S, N, and toxics. The objective is to provide the foundation for developing a

standard set of Forest Service AQRVs, sensitive receptors, indicators, and associated protocols to guide field studies on AQRVs nationwide.

Both chemical and biological sensitive receptors are assessed. Emphasis is placed primarily on acidification and eutrophication effects associated with deposition of S and N, and secondarily on effects associated with Hg, pesticides, or other toxic materials. The AQRV protocol development work is intended to occur in two phases. During Phase I, which is the subject of this report, we focus mostly on indicator selection, and the ways in which indicators can or cannot be used for assessment purposes. We also provide a summary of a number of existing protocol documents which may be helpful in refining the Forest Service AQRV program. We conducted an initial scoping of appropriate field and laboratory methods for high-priority indicators. To this end, we highlight selected existing field and laboratory protocols documents prepared for the Forest Service and other federal agencies. Phase II, planned for initiation at a later date, will include more detailed evaluation, and recommendation, of specific protocols.

Air pollution receptors and associated AQRVs have been identified as sensitive attributes of aquatic and terrestrial ecosystems. A wide range of AQRVs and sensitive receptors have been identified by individual forests, based on previous research and protocols development efforts as summarized by the Forest Service Air Program (www.fs.fed.us/air/ technical/class1/index.htm). Both biological and chemical attributes have been recommended as sensitive receptors, including such considerations as sensitivity to air pollution damage, logistical factors associated with field sampling (especially in wilderness areas), cost, and field staff training requirements. One of our objectives here is to recommend a suite of indicators that together reflect the cumulative impacts of changing air quality on ecosystem health. We attempt to focus on indicators that are relatively independent of effects from other stressors, but also to recognize and to point out linkages where they occur with such factors as climate change, fire, land management, and insect infestation.

Federal Land Managers (FLMs) are required by the Clean Air Act and other federal legislation to determine whether proposed development upwind of Class I areas poses substantial threat to AQRVs. High quality data are needed on the status and trends of AQRVs because:

- Rather small changes in chemical condition can have important effects on biota.
- Natural variability is often high, complicating efforts to assess resource sensitivity or effects.
- Sensitive aquatic ecosystems often exhibit dilute water chemistry, which is difficult to analyze with the level of accuracy needed.

- Potential costs are high to the regulated community and to the environment if mistakes are made in the collection, analysis, or interpretation of environmental data. Resulting data are frequently used in litigation, requiring a high level of quality assurance.

Past and current inventory and monitoring approaches have focused on an array of issues, including habitat evaluations, resource surveys, site condition inventories, and watershed analyses. As a consequence, a wide variety of databases have been created within the Forest Service. It is often difficult to share data among administrative units, due in part to differences in data collection methods and study objectives (Potyondy et al. 2006). Varying approaches may fail to satisfy Agency requirements regarding the development of credible, consistent, and understandable data regarding natural resource sensitivity and effects of air pollutants.

Where appropriate, standard national protocols should be considered for possible adoption by the Air Program for collecting, processing, and interpreting data regarding the effects of atmospheric deposition on natural resources on Forest Service lands. The use of standardized protocols would foster consistency across individual forests and maximize the Agency's ability to assess spatial and temporal trends in resource sensitivity and environmental effects. Use of consistent approaches in the collection and interpretation of environmental data would help efforts to understand cause/effect relationships among air pollution, biogeochemistry, natural resource sensitivity, and land management.

There are several purposes to this report. We attempt to:

1. provide background information on air quality related values (AQRVs) and associated sensitive ecological receptors that are most generally applicable throughout Forest Service lands;
2. provide an organized structure for investigation of the most readily-documented and important effects of atmospheric deposition;
3. recommend a suite of national attributes to be investigated in conjunction with AQRV assessment in order to maximize consistency of approach;
4. identify examples of existing standardized protocols for field sampling, laboratory analysis, and data analysis and screening that could be considered in formulating Agency-wide protocols; and
5. make recommendations regarding development of a formal process for selection of appropriate protocols for nationwide implementation.

National protocols should be selected based on consideration of several criteria, including the following (Potyondy et al. 2006):

1. protocol is scientifically based,
2. protocol is repeatable,
3. an important attribute of the ecosystem is measured by the protocol, and
4. protocol is generally accepted and widely used by the scientific research community.

It must, however, be recognized that there will not be a single appropriate protocol in every situation that will efficiently characterize an important attribute nationwide. Some attributes and site characteristics are sufficiently variable from region to region that multiple protocols may be most appropriate. Nevertheless, adoption where possible of national-scale standards for data gathering will allow data to be compared across forest and regional boundaries and will provide information that is needed for national assessments and decision-making.

Aquatic effects research on Forest Service lands focuses on both lakes, mainly in the western U.S., and streams, mainly in the eastern U.S. To the extent practical, sensitive attributes and protocols should be selected that are applicable to both lakes and streams, and throughout most or all regions of the U.S. Similarly, forest effects studies have focused on both coniferous and deciduous forest types. In this report, we address questions concerning which of the existing AQRVs, and associated field, laboratory, and data analysis protocols, are most useful, practical, and cost-effective for meeting Forest Service air program objectives. Important considerations include:

1. faint signal-to-noise ratio, especially in terrestrial ecosystems and in western aquatic ecosystems;
2. confounding stressors, especially climate, insect infestation, fire, introduced species, and legacy effects of past land use;
3. constraints of sampling in wilderness areas due to wilderness rules regarding access by mechanized equipment and travel distances;
4. constraints regarding laboratory analytical holding times;
5. national and regional applicability;
6. cost and training constraints;
7. quality control issues and necessity of passing peer-review.

2. APPROACH

The approach to this scoping study entailed the following elements:

1. Literature review. We reviewed available literature on AQRVs and related protocols and also on critical loads approaches. This review process included peer-reviewed publications, agency reports, websites, and other documents.
2. Agency survey. We contacted by telephone and/or email a group of Forest Service scientists who work in the field of aquatic and terrestrial effects of acidic deposition. The purpose of these contacts was to obtain feedback on our draft list of recommended AQRVs and to obtain copies of pertinent manuscripts and reports on the topic of this research effort.
3. AQRV prioritization. Based on results of our review of existing information, we compiled a list of AQRV attributes that we recommend for Forest Service monitoring of aquatic and terrestrial ecosystems potentially impacted by acidic deposition. These include specific sensitive receptors and indicator criteria.
4. Data analysis. We provide recommendations for critical loads analysis for N and S deposition. We also provide recommendations for screening analyses to aid in the identification of resources that are likely to be sensitive to air pollution degradation.

3. RESULTS

3.1. Potential Air Pollution Stressors

A variety of air pollutants have the potential to stress aquatic and terrestrial ecosystems. Both the pollutants and the types of potential effects are variable. For this report, we focus mostly on atmospheric pollutants that contribute to soil and/or water acidification and eutrophication (nutrient enrichment). Both atmospheric S and N have the potential to cause acidification. Atmospheric N can also cause eutrophication where N supply is limiting. We also address, with lesser coverage, the effects on biological resources of atmospheric contributions of Hg and other toxic materials.

Large areas throughout the United States contain substantial populations of low-ANC lakes and streams. These include much of the Northeast, mid-Appalachian Mountains, southern Appalachian Mountains, northern Florida, Upper Midwest, and the western United States. The eastern states include many acidified surface waters that have been impacted by acidic deposition. The western United States contains many of the surface waters most susceptible to potential acidification effects, but the levels of acidic deposition in the West are generally low and acidic surface waters are rare (Charles 1991, Sullivan 2000). Many of these areas, especially in the northeastern United States and Appalachian Mountains, also contain extensive areas with acid-sensitive soils. Most fresh waters in the United States are phosphorus (P)-limited and are therefore not sensitive to nutrient enrichment effects from N deposition. However, some freshwaters in the United States appear to be N-limited. They mostly occur in remote locations

at relatively high elevation, especially in the western United States. These N-limited lakes and streams are sensitive to nutrient enrichment effects from N deposition.

The geologic composition of a region plays a dominant role in influencing the chemistry, and therefore the sensitivity, of surface waters and soils to the effects of acidic deposition. Bedrock geology formed the basis for a national map of surface water sensitivity (Norton et al. 1982) and has been used in numerous acidification studies of more limited extent (e.g., Gibson et al. 1983, Dise 1984, Bricker and Rice 1989, Stauffer 1990, Stauffer and Whittchen 1991, Vertucci and Eilers 1993, Sullivan et al. 2007). Most of the major concentrations of low ANC surface waters are located in areas underlain by bedrock resistant to weathering. Other factors in addition to geology contribute to the sensitivity of surface waters to acidic deposition, including soil chemistry, land use, and hydrologic flowpath..

Land use influences watershed sensitivity to acidification mainly through land disturbance and exposure of S-bearing minerals to oxidation, loss of base cations through erosion and/or timber harvesting, and change in N status of the forest through timber management. Each of these types of activity can influence the relative availability of mineral acid anions (sulfate [SO_4^{2-}], nitrate [NO_3^-]) and the amount of base cations (calcium [Ca^{2+}], magnesium [Mg^{2+}], potassium [K^+], sodium [Na^+]) on the soil ion exchange sites and in drainage water. The balance between mineral acid anions and base cations in solution, in turn, affects the ANC and pH of soil water and surface waters.

The movement of water through the soils and bedrock, into a lake or stream, and the interchange between drainage water[1] and the soils, rock, and sediments regulate the type and degree of watershed response to acidic inputs (Sullivan 2000). Surface waters in the same setting can have different sensitivities to acidification depending on the relative contributions of near-surface drainage water and deeper groundwater (Eilers et al. 1983, Chen et al. 1984, Driscoll et al. 1991). Acidic deposition that falls as precipitation directly on the lake surface, may eventually be neutralized by in-lake reduction processes which are controlled in part by hydraulic residence time (Baker and Brezonik 1988). Natural hydrologic events also alter acidification and neutralization processes during snowmelt and change flowpaths during extended droughts (Webster et al. 1990).

Watershed processes control the extent of ANC contribution from soils to drainage waters as acidified water moves through undisturbed terrestrial systems. These processes

[1] Drainage water refers to water that moves through watershed soils and into a stream, and perhaps into a lake.

regulate the extent to which drainage waters will be acidified in response to acidic deposition. Of particular importance is the concentration of acid anions in solution, including SO_4^{2-}, NO_3^-, and organic acid anions. Naturally-occurring organic acid anions, produced in upper soil horizons, normally precipitate out of solution as drainage water percolates into the deeper mineral soil horizons. Soil acidification processes reach an equilibrium with acid neutralization processes at some depth in the mineral soil (Turner et al. 1990). Drainage waters below this depth generally have high ANC. Acidic atmospheric deposition allows the natural soil acidification and cation leaching processes to occur at greater depths in the soil profile, allowing water that is rich in SO_4^{2-} or NO_3^- to flow from mineral soil horizons into drainage waters. If these anions are charge-balanced by H^+ and/or Al^{n+} cations, the water will have low pH and could be toxic to aquatic biota. If they are charge-balanced by base cations, the pH of the water will be higher but the base cation reserves of the soil can become depleted.

3.1.1. Sulfur

Sulfur deposition moves through watershed soils and into surface waters in anionic form, as SO_4^{2-}. Sulfate is the most important anion contributed by acidic deposition in most, but not all, parts of the United States. In some regions (notably the glaciated Northeast, Upper Midwest, and West), much of the deposited S moves readily through soils into streams and lakes. Thus, SO_4^{2-} has been classified as a mobile anion (Seip 1980). However, SO_4^{2-} is less mobile in some areas, most notably the unglaciated southeastern United States. The extent of SO_4^{2-} mobility is an important factor governing the extent to which S deposition contributes to soil and water acidification, base cation depletion, and aluminum (Al) mobilization, each of which can harm sensitive ecosystems.

3.1.2. Nitrogen

Nitrate (and also ammonium [NH_4^+] which can be converted to NO_3^- within the watershed) has the potential to acidify soils, soil waters, and surface waters. However, N is a limiting nutrient for plant and microbial growth in most terrestrial, and some aquatic, ecosystems. Therefore, atmospheric N deposition has the potential to contribute to increased productivity, eutrophication, and N-saturation in remote locations (Baron et al. 2000, Sickman et al. 2001, Williams and Tonnessen 2000). Forest soils usually leach relatively little NO_3^- into surface waters. For that reason, increased atmospheric deposition of N does not necessarily cause

adverse aquatic environmental impacts. In many areas, added N is taken up by terrestrial biota and the most visible effects include an increase in forest productivity (Kauppi et al. 1992) and competitive shifts among plant species based on their N requirements. However, in some areas, especially at high-elevation sites, terrestrial ecosystems have become N-saturated and high levels of deposition cause elevated levels of NO_3^- in drainage waters (Aber et al. 1989, 1998; Stoddard 1994). Enhanced leaching of NO_3^- can cause depletion of base cations from forest soils, adverse impacts on sensitive tree species, and acidification of drainage waters in base-poor soils.

High concentrations of lake or streamwater NO_3^-, which may be indicative of ecosystem N saturation, have been found at a variety of locations throughout the United States, including the San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al. 1996), the Front Range of Colorado (Baron et al. 1994, Williams et al. 1996), the Allegheny Mountains of West Virginia (Gilliam et al. 1996), the Catskill Mountains of New York (Murdoch and Stoddard 1992, Stoddard 1994), and the Great Smoky Mountains in Tennessee (Cook et al. 1994).

Atmospheric deposition of nutrients is expected to increase in the future in remote areas that are situated down-wind from centers of agricultural and/or human population growth. In particular, high-elevation areas in the Sierra Nevada and Rocky Mountains are susceptible to such increases in nutrient deposition (Fenn et al. 2003, Sickman et al. 2003b). In some areas, atmospheric N deposition has been linked with eutrophication of high-elevation lakes (c.f., Sickman et al. 2003a, Melack et al. 1989).

3.1.3. Toxics

Mercury (Hg) is naturally occurring and is found throughout the environment. Mercury present in fossil fuels is released to the atmosphere during combustion, and is subsequently available for long-range atmospheric transport and deposition to the earth surface. It enters lakes and rivers from atmospheric deposition of the Hg emitted by air pollution sources and also from nonpoint sources via erosion and runoff.

Mercury is a toxin that can damage the human brain and nervous system. The developing fetus and young children are particularly susceptible to the toxic effects of Hg. Human exposure to Hg mostly occurs via consumption of fish and other seafood that has accumulated high concentrations of Hg. Fish consumption advisories for various lakes and rivers have been issued in most states throughout the U.S.

Monitoring studies to evaluate the extent to which atmospheric deposition of Hg affects aquatic ecosystems on Forest Service lands could focus on the concentrations of total and/or methyl Hg in water, invertebrates, fish, or piscivorous birds. Alternatively, methylation rates within different environmental compartments might be quantified. Ultimately, the effects of concern regarding atmospheric Hg deposition include physiological or central nervous system effects on piscivorous birds and humans who consume large quantities of fish that have accumulated high levels of Hg.

Pesticides applied to agricultural crops can become volatized or suspended in the atmosphere with dust particles, and eventually be transported with prevailing winds to remote areas. For example, in 2003, there were 63 million pounds of active pesticide ingredient applied to agricultural lands in Fresno, Kern, and Tulane Counties in California. These counties are immediately upwind of national forest and park lands in the Sierra Nevada. Organophosphates have been detected in precipitation at elevations up to 1,920 m in Sequoia National Park (Zabik and Seiber 1993) and measured in plant foliage across a range of elevations (Aston and Seiber 1997). The effects of atmospheric deposition of pesticides at remote locations are poorly known. In particular, however, there is concern that fungicide deposition could harm sensitive lichen species (McCune et al. 2006).

There are a variety of other toxic chemicals that can be atmospherically deposited, some of which have the potential to bioaccumulate. These include Polychlorinated biphenyls (PCBs) and some fire retardant chemicals. In addition, air quality can affect natural resources through mechanisms other than atmospheric deposition of acidifying, eutrophying, or toxic substances. Especially important in this regard within some regions of the country are effects of air pollutants on visibility and on the generation of ground level (trophospheric) ozone (O_3).

3.1.4. Other Pollutants

Visibility and consequent visitor enjoyment of scenic vistas, can be degraded by both natural processes and air pollutants. Visibility degradation is caused by the scattering and adsorption of visible light by particles and/or gasses in the atmosphere. Important light-scattering pollutants include SO_4^{2-} and NO_3^- particles and NO_2 gas. Congress passed the Regional Haze Rule in 1999, which requires states to develop and implement plans to make continuous progress toward the national goal of zero human-caused visibility degradation in Class I national park and wilderness areas by 2064. Therefore, visibility is monitored at many

locations, mainly through the Interagency Monitoring of Protected Visual Environments (IMPROVE) Program.

Ozone in the troposphere forms by interactions of sunlight with two different kinds of atmospheric constituents: NO_x and volatile organic compounds (VOCs). The VOC category includes thousands of different organic compounds that can be volatilized. Important human-caused sources of VOCs include motor vehicle exhaust, gasoline vapors, and vapors from paints, solid waste, and various commercial and industrial processes. Vegetation also emits VOCs that participate in the formation of O_3.

Neither visibility effects nor O_3 effects are directly caused by atmospheric deposition. Rather, both are caused partly by atmospheric concentrations of air pollutants and partly by atmospheric concentrations of natural constituents. Neither of these issues is addressed in this report.

3.2. Type of Effect

3.2.1. Acidification

Atmospheric inputs of both S and N can cause acidification of soil, soil water, and fresh drainage water (lakes, streams). In most regions of the United States that have experienced acidification impacts from air pollution, those impacts have mainly been due to S deposition. There are also, however, some regions, especially in the western U.S., where resources are more threatened by N inputs than by S inputs. This is at least partially due to the very low levels of S deposition received at many western locations. There are also regions (portions of the Northeast, West Virginia, high elevations in North Carolina and Tennessee) where both atmospheric S and N contribute substantially to the observed acidification.

Acidification from S and N deposition can have several important chemical and biological effects. In particular, there are changes in the acid-base status of surface and soil water which can cause short-term or long-term toxicity to aquatic or terrestrial biota. An environmental stressor that changes the natural processes that occur in the soil can adversely impact plant species composition and water storage and discharge in forested ecosystems. Deposition of S and N from the atmosphere can change nutrient (e.g., Ca^{2+}, Mg^{2+}, K^+, N) availability, rates of organic matter decomposition, mobilization of metals (including Al) to soil solution, and microbial activities in the soil. Acidic deposition usually increases the concentration of SO_4^{2-} and/or NO_3^- in drainage water. These anions are charge-balanced by

cations derived from the soil cation exchange complex or released through mineral weathering. The cations can include base cations such as Ca^{2+} and Mg^{2+} and acid cations such as H^+ and Al^{n+}. When the concentration of H^+ and/or Al^{n+} in drainage water increases, toxic conditions may result. Increased H^+ concentration (reduced pH) affects different species of aquatic biota at different levels. Some species are affected at pH levels near 6.0, whereas others can be quite tolerant of pH values below 5.0. Many species of fish are adversely affected at H^+ concentrations greater than about 10 μeq/L (pH 5.0). Depending on concentration, inorganic Al in solution can also be toxic to both aquatic organisms and plants.

Aluminum occurs naturally in soils. It has a pH-dependent solubility in water. Solubility increases dramatically at pH values below about 5.5. One of the most important effects of acidic deposition on watersheds has been increased mobilization of Al from soils to surface waters (Cronan and Schofield 1979). Al concentrations in acidified drainage waters are often an order of magnitude higher than in circumneutral waters. Potential effects of Al mobilization to surface and soil waters include alterations in nutrient cycling (Dickson 1978, Eriksson 1981), pH buffering effects (Driscoll and Bisogni 1984), toxicity to aquatic biota (Schofield and Trojnar 1980, Muniz and Leivestad 1980, Baker and Schofield 1982, Driscoll et al. 1980), and toxicity to terrestrial vegetation (Ulrich et al. 1980). Inorganic Al concentrations often increase with decreasing pH, and reach potentially toxic concentrations (> ~2 μM) in surface drainage waters having pH less than about 5.5.

Aluminum toxicity to fish varies according to species and life-stage. Young fish are often more sensitive than older fish. Aluminum disrupts the functioning of fish gills and inhibits respiration and ion regulatory activities (Howells et al. 1990). Wigington et al. (1993) found 50% brook trout mortality for *in situ* exposure experiments at median inorganic monomeric Al (Al_i) concentrations of about 200 μg/L (7.4 μM). For prolonged exposures, greater than eight days, having Al_i continuously above various threshold levels, 50% mortality was found for Al_i threshold values between 100 and 200 μg/L (3.7 to 7.4 μM). Blacknose dace were somewhat more sensitive to Al exposure; 50% mortality was observed at a median Al_i concentration of 120 μg/L (4.4 μM). Sculpin were less sensitive and showed 50% mortality at Al_i concentrations ranging from 200 to 300 μg/L (7.4 to 11.1 μM).

Aluminum is also toxic to tree roots, although much higher concentrations of Al in soil solution are required in order to elicit a toxic response as compared with the toxicity of Al to fish. Plants affected by Al often have reduced root growth, which restricts the ability of the plant

to take up water and nutrients (Parker et al. 1989). Calcium is well known as an ameliorant for Al toxicity to roots, as well as to fish. Magnesium, and to a lesser extent Na^+ and K^+, have also been associated with reduced Al toxicity. Critical levels of atmospheric S or N deposition that will protect sensitive forest resources from damage are often based in part on the molar ratio of Ca^{2+} to Al in solution as an indicator of increased potential for toxic response. Damaged forest stands often exhibit Ca:Al < 1.0 (Ulrich 1983, Schulze 1989, Sverdrup et al. 1992).

Base cations, including Ca^{2+}, Mg^{2+}, and K^+, are nutrients that are taken up through plant roots in dissolved form. A large fraction of the base cation stores in rocks and soils are bound in mineral structures and are unavailable to plants. The pool of dissolved base cations in the soil is adsorbed to negatively charged exchange sites. These exchangeable cations can become desorbed in exchange for H^+ or Al^{3+}. Weathering gradually breaks down rocks and minerals to replenish the pool of adsorbed base cations. Base cation reserves are gradually leached from the soils in drainage water, and this leaching is enhanced by acidic deposition.

Leaching of base cations by acidic deposition can deplete the soil of exchangeable bases faster than they are resupplied via weathering (Cowling and Dochinger 1980). The importance of this response has been recognized because some watersheds are not exhibiting much ANC and pH recovery of drainage water in response to recent decreases in S deposition. This limited recovery can be at least partially attributed to decreased base cation concentrations in surface water. This understanding has developed slowly. During the 1980s, the generally accepted paradigm of watershed response to acidic deposition was analogous to a large-scale titration of ANC (Henriksen 1980). Atmospheric input of acidic anions was believed to result in movement of those anions through soils into drainage waters with near stochiometric loss of surface water ANC. This view was modified by Henriksen (1984), who suggested that a modest component of the added SO_4^{2-} (up to a maximum of about 40%) could be charge-balanced by increased mobilization of base cations from soils, and the remaining 60 to 100% of the added SO_4^{2-} resulted in loss of ANC in surface waters. During the latter part of the 1980s, it became increasingly clear that a larger component (>40%) of the added SO_4^{2-} was in fact neutralized by base cation release in most cases and the ANC (and therefore also pH) of surface waters typically did not change as much as was earlier believed. This understanding developed in large part from paleoecological studies (e.g., Davis et al. 1988, Charles et al. 1990, Sullivan et al. 1990a), which indicated that past changes in lakewater pH and ANC had been small relative to estimated increases in lakewater SO_4^{2-} concentrations since pre-industrial times (Sullivan 2000). The

belief that changes in acidic deposition were accompanied mainly by changes in ANC and pH has been replaced by the realization that changes in SO_4^{2-} were accompanied mainly by changes in base cations. Thus, surface waters have not been acidified as much by historical deposition as was earlier believed. Furthermore, surface water ANC and pH should not be expected to recover quickly upon reduced emissions and deposition of S and N.

As aquatic effects researchers have revised their understanding of the quantitative importance of the various acidification processes, terrestrial effects researchers have also turned greater attention to the importance of the response of base cations to acid deposition and the interactions between base cations (especially Ca^{2+} and Mg^{2+}) and Al (Sullivan 2000). Likens et al. (1996) showed that acidic deposition enhanced the release of base cations from forest soils at Hubbard Brook Experimental Forest (HBEF) from the mid-1950s until the early 1970s. As the pool of base cations in soil became depleted, concentrations in streamwater decreased from 1970 through 1994 by about one-third. The decrease in base cation deposition inputs coupled with this increase in soil release of base cations may have depleted soil pools to the point where ecosystem recovery from decreased S deposition will be seriously delayed. Likens et al. (1996) also suggested that documented declines in forest biomass accumulation at HBEF might be attributable to Ca^{2+} limitation or resulting Al toxicity.

3.2.2. Eutrophication

Eutrophication, or nutrient enrichment, is a potential consequence of N deposition to both aquatic and terrestrial ecosystems. Many freshwater ecosystems are phosphorus (P)-limited, and therefore would not be expected to increase primary productivity in response to increased atmospheric inputs of N. However, there are examples of fresh waters which appear to be N-limited or N and P co-limited (e.g., Baron 2006). In such aquatic systems, atmospheric inputs of N would be expected to increase productivity and/or alter biological communities such as phytoplankton.

Estuaries and other coastal ecosystems are also susceptible to nutrient enrichment, especially from N. Land clearing, agricultural land uses, sewage treatment discharge, and atmospheric deposition can all result in high loadings of N to the coastal zone. Excessive N inputs can contribute to a range of impacts, including enhanced algal blooms, decreased distribution of seagrasses and decreased dissolved oxygen (DO) concentration (Valiela et al. 1992, Nixon 1995, Borum 1996, Bricker et al. 1999, Kopp and Neckles 2004). Because of

human population growth and the great popularity of coastal areas, there is substantial potential for increased N loading to coastal ecosystems. Atmospheric deposition of N contributes to that load, but is generally not the major source of estuarine N. AQRVs for protection of estuarine ecological conditions are beyond the scope of this study. Protocols for monitoring estuaries and other coastal areas are therefore not addressed in this report.

Nitrogen deposition also poses risk of nutrient enrichment to terrestrial ecosystems. The growth of trees in temperate forests is often N-limited. As a consequence, an important result of increased N deposition can be enhanced forest growth (Kauppi et al. 1992). Such growth enhancement can potentially exacerbate other nutrient deficiencies, such as Ca^{2+} or Mg^{2+}, thereby causing problems with forest health.

Nitrogen deposition can affect the relative abundance and competitive interactions of herbaceous plant species, and these effects can be especially pronounced in alpine and other grassland ecosystems and in wetlands. Such changes in interspecies competition can change the vegetative character of these ecosystems in ways that are not well understood.

3.2.3. Bioaccumulation and Toxicity

Atmospheric deposition can contribute to toxicity responses in several ways. The atmospheric pollutants of concern with respect to toxicity are primarily Hg and pesticides. Atmospheric deposition is an important component of Hg cycling and biogeochemistry. Mercury is known to bioaccumulate in aquatic organisms, reaching potentially high concentrations in larger, piscivorous fish. Such Hg bioaccumulation is an important human health concern, especially among subpopulations of people who consume large quantities of fish. Pesticides and other toxics (including PCBs and fire retardant chemicals) can be air deposited and can bioaccumulate in predator species. The degree of bioaccumulation is generally a function of the age of the organism and its position in the food web. Older individuals at the top of the food web bioaccumulate more Hg and toxics than do younger individuals nearer to the bottom of the food web.

3.3. AQRVs and Sensitive Receptors

There are three ecological AQRVs on Forest Service land that are susceptible to air quality degradation: surface water, soil, and flora. There are a variety of potentially important sensitive receptors for each AQRV. Sensitive receptors for effects on surface water could include

water chemistry, productivity, and the response of important life forms, including fish, zooplankton, benthic macroinvertebrates, and phytoplankton. Key sensitive receptors for assessing impacts on soil include soil chemistry and soil solution chemistry. Sensitive receptors for flora include macro-lichens and acid-sensitive vascular plant species. In particular, evidence has accumulated that suggests adverse impacts from acidic deposition on red spruce and sugar maple at some locations in the eastern United States. The picture is less clear for effects of deposition on western trees, although some common western tree species (mainly Ponderosa and Jeffrey pine) are known to be sensitive to O_3 damage (not reviewed in this report).

3.3.1. Surface Water

Aquatic systems can be subdivided into major components based on hydrology. At the broadest level, aquatic ecosystems can be classified as riverine, lacustrine, and palustrine systems (Cowardin et al. 1979). Riverine systems can be identified at varying scales, including valley segment, river reach, and channel unit. Lacustrine systems include deepwater habitats associated with lakes and reservoirs. According to Cowardin et al. (1979), these are larger than 8 ha in surface area and > 3 m deep. However, various national surveys have defined lakes as being larger than 1 ha or 4 ha, depending on the study (c.f., Landers et al. 1987, Paulsen 2006). The lower size cutoff is generally determined, at least in part, based on the resolution of available regional maps with which to designate the statistical sampling frame for the survey. Palustrine systems include small, shallow, or intermittent water bodies such as wetlands and ponds.

High mountain lakes and streams are good indicators of regional environmental change (Seastedt et al. 2004), partly because they integrate conditions within their watersheds, including atmospheric, edaphic, geologic, and hydrologic conditions. Also, high mountain aquatic ecosystems are removed from many of the human-caused pollution sources that are common at lower elevation. Land management agencies often focus on lakes and streams to estimate critical loads for atmospheric deposition, especially for S and N (Porter et al. 2005).

3.3.1.1. Water Chemistry

There are numerous sensitive chemical receptors that can be used to assess impacts of acidic deposition on lake or stream acid-base chemistry. These include surface water pH and concentrations of SO_4^{2-}, NO_3^-, Al^{n+}, Ca^{2+}, sum of base cations (SBC), and ANC. All of these are of interest, and each can provide useful information regarding both sensitivity to surface water

acidification and the level of acidification that has occurred. Acidification effects on aquatic biota are most commonly evaluated using either ANC or pH as the chemical indicator criterion. ANC is generally preferred, because of its greater stability and linearity, and because surface water acidification models do a better job projecting ANC than they do pH. ANC criteria have been widely used for evaluation of potential acidification effects on fish communities. The utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al_i.

The best single water chemistry indicator for both atmospheric deposition sensitivity and effects is the ANC. It can be determined by Gran titration or as the difference between the measured base cation and mineral acid anion concentrations:

$$ANC = (Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + NH_4\text{-}) - (SO_4^{2-} + NO_3^{-} + Cl^{-})$$

Field studies often rely upon the Gran titration approach. Process-based models, such as MAGIC, PnET-BGC, and NuCM utilize the ANC calculated from the charge balance. For monitoring and assessment purposes, it is always best to determine both titrated and calculated ANC values. The difference between the two can yield important information about data quality and reveal the influences of natural organic acidity and/or dissolved Al on the overall acid-base chemistry of the water. Furthermore, measurement of full ion chemistry is needed to provide sufficient information regarding:

1. the contribution of the various acidic anions (SO_4^{2-}, NO_3^{-}, Cl^{-}) to existing acidity;
2. the likelihood of confounding impacts other than acidic deposition, such as road salt contamination, acid mine drainage, natural organic acidity, or agricultural inputs of nutrients;
3. the quality of the database; and
4. possible base cation depletion of watershed soils.

Surface water pH is a common alternative to ANC as an indicator of acidification. However, at pH values above about 6.0, pH is not a good indicator of either sensitivity to acidification or level of impact. In addition, pH measurements (especially at these higher values) are sensitive to levels of dissolved CO_2 in the water. In contrast, ANC is more stable and it reflects sensitivity and effect in a linear fashion across the full range of ANC values. Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated and

calculated ANC values should be determined in field studies aimed at resource characterization or long-term monitoring.

An additional important indicator of potential impact on surface water chemistry is NO_3^- concentration. High lake or streamwater NO_3^- concentration, especially during the growing season, suggests the possibility of N-saturation from atmospheric N deposition or some other (i.e., fertilizer application) source of N.

3.3.1.2. Water Productivity

Excess contribution of N to aquatic ecosystems can stimulate algal productivity, which in turn can reduce DO levels. Extreme cases of DO reduction can cause oxygen depletion, fish mortality, odor problems, and other aspects of water quality degradation. The extent of effect is determined by the level of N input in combination with characteristics of the receiving body of water and its watershed. Especially important are the supply of P, which is often limiting in freshwater ecosystems, and light availability. The most common, and easiest to document, indicators of change in algal productivity are measures of water clarity and the concentrations of chlorophyll *a*. Clarity is also strongly influenced by erosional inputs of fine sediment to the lake or stream system. Chlorophyll *a* concentration is generally more directly tied to algal productivity than is water clarity.

3.3.1.3. Aquatic Biology

Changes in lake and stream acid-base chemistry, including pH, ANC, Al_i, and Ca^{2+}, can affect in-stream and in-lake biota. The organisms most likely to respond to such changes in water chemistry include fish, aquatic insects, zooplankton, and diatoms. In some cases, amphibians are also important sensitive biological receptors.

In most stream or lake survey areas, direct quantification of biological responses to surface water acidification is not possible, given the scarcity or absence of biological long-term monitoring and dose-response data. Few biological long-term monitoring studies have been conducted. Much of the available dose-response data have been generated from the U. S. Environmental Protection Agency's (EPA's) Episodic Response Project (ERP; Wigington et al. 1993), and studies of streams in Virginia and Great Smoky Mountains National Park and lakes in the Adirondack Mountains, New York. Data with which to evaluate acidification relationships have been scarce in most other regions.

3.3.1.3.1. Fish

Aquatic impacts of acidic deposition have been most thoroughly studied for fish. Effects of low pH and ANC on many individual fish species have been documented (Baker et al. 1990c). In particular, a great deal of research has focused on brook trout, an important native salmonid found throughout the eastern United States. Research in the West has been more limited and has focused more on cutthroat trout. Effects are often quantified by determining species presence/absence for salmonids, the condition factor of a particularly common and relatively acid-sensitive species, or the overall number of fish species that occur in the lake or stream reach.

The most common methods for determining the occurrence of fish species within a stream reach are electrofishing (Peterson et al. 2002, 2004) and snorkeling (Thurow 1994). Minimum survey length should be specified in relation to stream size rather than a pre-specified distance (Potyondy et al. 2006). Lyons (1992) found that electrofishing a length of stream equal to 20 times bankfull width, or 35 times wetted width, was sufficient to determine the presence of most fish species. Reynolds et al. (2003) reported that a sample reach equal to 40 times the mean wetted width was sufficient to capture >90% of the species in >90% of their Oregon low- and high-gradient study streams. If the fish detection probability is low, it may be necessary to sample longer reaches. Snorkel surveying can be substituted in clearwater streams, where electrofishing is not permitted (such as where an endangered species is present), or where fish injury is a concern.

Fish are sensitive to low pH and high Al_i. Attention is often focused on salmonid fish because of the perceived importance and popularity of salmonid fisheries. Salmon and some trout species (i.e., rainbow trout) are highly sensitive. Brook trout, although very important as a native species in many eastern streams, is more tolerant of high acidity. Fish species richness, population density, condition factor, age distribution, size, and bioassay survival have all been shown to be reduced in low-ANC streams as compared to intermediate-ANC and high-ANC streams (Bulger et al. 1995, Dennis and Bulger 1995, Dennis et al. 1995, MacAvoy and Bulger 1995). Fish species richness is a good indicator of acidification response. There is often a positive linear relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 μeq/L (Bulger et al. 1999, Sullivan et al. 2006). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, generally having smaller watersheds, to also support

fewer fish species, irrespective of acid-base chemistry. This is likely due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is one of the most useful indicators of biological effects of surface water acidification. Examples of research on this topic and other aspects of fish response to atmospheric deposition are presented in Appendix A.

It is expected that sublethal effects are manifested on an acid-sensitive aquatic species well before the species is eliminated from a particular lake or stream. For that reason, loss of an acid-sensitive species is not necessarily an ideal indicator of acid stress. Clearly, stress begins to occur prior to species elimination. Sublethal effects are more difficult to quantify, but are nevertheless important. Condition factor is one index of sublethal impact that has been applied to quantify sublethal effects of acidification on fish. Condition factor is an index to describe the relationship between fish weight and length. Expressed as fish weight/length^3, multiplied by a scaling constant, this index reflects potential depletion of stored energy reserves (Everhart and Youngs 1981, Goede and Barton 1990, Dennis and Bulger 1995). Field studies have shown lower condition factor in fish found in more acidic streams (Dennis and Bulger 1995, Webb 2003).

Measured fish tissue concentration of Hg, pesticides, or other bioaccumulative toxic chemicals is the common indicator of atmospheric deposition impacts from toxic materials. Toxic chemical concentrations can be expressed as mass of contaminant per unit mass of fish, based either on digested whole fish or on fillet samples. Whole fish digests are commonly used for small fish, whereas fillet samples are more commonly analyzed when the risk is considered to be primarily from human ingestion of large fish.

Much of the work conducted to date on the biological effects of acidification has been focused on fish. However, this focus has largely been the result of the value people place on fish and fishing, rather than any ecological consideration (Sullivan 2000). Algal, invertebrate, and other vertebrate communities are also sensitive to adverse impacts of acidification. However, lakes and streams show spatial and temporal variability in response to a host of biotic and abiotic factors. Against this background of variability, it is difficult to detect changes in biological communities in response to an individual environmental stressor without long-term biological data (Schindler 1990, Lancaster et al. 1996). Long-term data sets are rare, and there are few well-documented instances of temporal changes in biological communities in response to changes in water chemistry. Regardless, it is known that surface water acidification affects

virtually all trophic levels (e.g., Flower and Battarbee 1983, Økland and Økland 1986, St. Louis et al. 1990, Rundle and Hildrew 1990, Simonin et al. 1993, Ormerod and Tyler 1991, Lancaster et al. 1996, Sullivan 2000).

Studies in the United States, Canada, and Europe have illustrated the feasibility and complexity of biological recovery in response to decreased acidity. Biological recovery of previously acidified lakes or streams can lag behind chemical recovery because of such factors as (a) other environmental stresses (Gunn 1995; Havas et al. 1995; Jackson and Harvey 1995; McNicol et al. 1995; Yan et al. 1996a,b); (b) barriers imposed by water drainage patterns (Jackson and Harvey 1995); and (c) the influence of predation (McNicol et al. 1995).

Populations of many species of amphibians have declined or become eradicated throughout the world in recent decades (Barinaga 1990, Wake 1991). The causes have not been evident and some of the declines have occurred in remote pristine areas. For example, in the Sierra Nevada, at least two of five species of aquatic-breeding amphibians, *Rana muscosa* (mountain yellow-legged frog) and *Bufo canorus* (Yosemite toad), have been declining (Phillips 1990). A number of hypotheses have been proposed for amphibian decline, including acidic deposition. In the western United States, however, acidic deposition has been discounted as the primary cause of the decline of *R. muscosa* and *B. canorus* in the Sierra Nevada and of *R. pipiens* and *B. boreas* in the Rocky Mountains (Corn et al. 1989, Bradford et al. 1992, Corn and Vertucci 1992).

In some cases, population fragmentation as a consequence of fish predation may be a more likely cause of amphibian decline (Bradford et al. 1993). It is generally recognized that *R. muscosa* was eliminated by introduced fish early in the 20th century in many lakes and streams in Sequoia and Kings Canyon National Parks. The amphibians have been eliminated from nearly all waters inhabited by fish, presumably by predation on tadpoles. Prior to 1870, virtually all of the high-elevation (> 2,500 m) lakes in the Sierra Nevada were barren of fish, but have since been stocked with fish by people. Fish introductions may have contributed to recent amphibian declines because amphibian populations are now more isolated from each other than formerly. The role of atmospheric deposition is not clear.

3.3.1.3.2. Benthic Macroinvertebrates

Within stream systems, macroinvertebrate communities are among the most sensitive attributes to disturbances, including those associated with atmospheric deposition (Cairns and

Pratt 1993). In addition, they are relatively easy to sample in the field (Karr and Chu 1999, Potyondy et al. 2006, Resh et al. 1995, Plafkin et al. 1989). Benthic macroinvertebrates are generally not included in lake biomonitoring. Macroinvertebrate samples are generally collected in streams using kick nets, which are placed immediately downstream from a sampling frame. Stones are selected within the frame and rubbed to dislodge the attached organisms, which are then washed into the net. Collected individuals are subsequently identified to the lowest practicable level, usually genus or family (Vinson and Hawkins 1996).

It has been well-documented that low streamwater pH can be associated with reductions in invertebrate density (Hall et al. 1980, Townsend et al. 1983, Aston et al. 1985, Burton et al. 1985, Kimmel et al. 1985), and also species richness or diversity (Townsend et al. 1983, Raddum and Fjellheim 1984, Kimmel et al. 1985, Burton et al. 1985, Hall and Ide 1987, Rosemond et al. 1992, Peterson and van Eeckhaute 1992, Sullivan et al. 2003). Effects on invertebrate density are not universal; a number of studies have found no density effects (Harriman and Morrison 1982, Simpson et al. 1985, Ormerod et al. 1987, Winterbourn and Collier 1987). However, a decrease in species richness with decreasing pH has been found in almost all such studies (Rosemond et al. 1992), and this finding has been especially pronounced in streams for order Ephemeroptera (mayflies). For example, Porak (1981) found that all species of mayfly were intolerant of the acid condition in the streams containing acidic Anakeesta leachates. Trichoptera (caddisflies) are also highly sensitive.

The Ephemeroptera-Plecoptera-Tricoptera (EPT) Index is a common measure of stream macroinvertebrate community integrity. The EPT metric is the total number of families present in those three insect orders (mayflies, stoneflies, and caddisflies, respectively). The total number of families is generally lower at acidified sites because the various families tend to exhibit varying acid sensitivity (c.f., SAMAB 1996). Mayflies tend to be most sensitive of the three, and stoneflies tend to be least sensitive (Peterson and Van Eeckhaute 1992).

3.3.1.3.3. Zooplankton

Sullivan et al. (2006) found that zooplankton taxonomic richness varied with ANC in Adirondack lakes (Table 1). Taxonomic richness, expressed as number of species of crustaceans, rotifers, and total zooplankton, increased with increasing ANC. In general, lakewater ANC explained nearly half of the variation in total zooplankton and crustacean taxonomic richness, but less for rotifer richness. These results (Table 1) provide the basis for

Table 1. Observed relationships between zooplankton species richness (R) and lakewater ANC. (Source: Sullivan et al. 2006)

Taxonomic Group	Equation	r^2	p
Total Zooplankton	R=15.65 + 0.089ANC	0.46	0.001
Crustaceans	R=6.35 + 0.028ANC	0.47	0.001
Rotifers	R=9.04 + 0.053ANC	0.30	0.001

estimating changes in zooplankton richness in response to past or future changes in lakewater ANC. Several zooplankton species found in lakes in the Sierra Nevada are also known to be sensitive to acidity status (Melack et al. 1989, Gerritsen et al. 1998).

3.3.1.3.4. Diatoms

Diatoms are excellent indicators of environmental change in aquatic ecosystems, including acidity, nutrient status, salinity, and climatic features (Stoermer and Smol 1999, Sullivan and Charles 1994). There are thousands of different species, many of which have rather narrow ecological tolerance ranges. Diatoms have been widely used as indicators of lake acidification. Inference based on diatom fossil remains preserved in lake sediments is an excellent approach for quantifying historical chemical change (Charles and Norton 1986).

Paleolimnological reconstructions of past lakewater chemistry are based on transfer functions derived from relationships between current lakewater chemistry and diatom (or, in some cases, chrysophyte) algal remains in surface sediments. Predictive relationships are developed using regional lake datasets, and are then applied to diatom assemblage data collected from horizontal slices of lake sediment cores to infer past lakewater conditions (Husar et al. 1991, Charles et al. 1989).

Diatoms can also serve as indicators of nutrient enrichment of rivers and streams. The USGS National Water Quality Assessment (NAWQA) Program collects physical and biological data from rivers across the United States (Gurtz 1993; http://water.usgs.gov/nawqa/). Benthic diatom samples were collected and analyzed at nearly 900 sites during the 1990s (Potapova and Charles 2002). These data illustrate several important ecological gradients, including downstream patterns of change from fast-flowing oligotrophic streams to low-elevation eutrophic rivers, acidity patterns, and temperature patterns (Potapova and Charles 2002)

Baron et al. (2000) and Wolfe et al. (2001) reported historical changes in diatom communities of high-elevation lakes in Colorado that might be attributable to increases in atmospheric N deposition. They found that small diatom taxa associated with oligotrophic conditions were replaced after about 1950 by larger taxa indicative of mesotrophic conditions. Estimated atmospheric N deposition in 1950 was then used as an estimate of N critical load. Similarly, Sickman and co-workers are currently developing a trophic-state inference model for the Sierra Nevada, based on diatom remains in lake sediments. This will be applied to lakes located along atmospheric N deposition gradients in Yosemite, Sequoia, and Kings Canyon national parks to reconstruct lakewater N concentrations over the past one to two centuries. Diatom indicators of trophic state will be compared to sedimentary reconstructions of historic N deposition in order to derive preliminary estimates of critical N loading to aquatic ecosystems in the Sierra Nevada. Under this type of approach, the critical load for N deposition is considered to be the deposition load at which measurable changes occur to diatom communities.

3.3.1.3.5. Amphibians

Amphibians are generally considered to be highly sensitive to changes in environmental conditions, and some species have likely been adversely impacted by acidic deposition in some areas. Furthermore, several species of amphibian have exhibited marked declines in abundance throughout the western United States in recent decades, and there has been much speculation concerning the cause(s) of these declines in abundance. Although acidic deposition may play a role in some areas, there is no evidence to suggest that it is a primary factor. Other issues, including fish introductions, are likely more important as stressors on amphibian populations across broad regional to national scales.

3.3.2. Soil

3.3.2.1. Effects of Acidic Deposition on Base Cation Supply

Calcium and other base cations are major components of soil water and surface water acid-base chemistry, and are also important nutrients that are taken up through plant roots in dissolved form. Base cations are typically found in abundance in rocks and soils, but a large fraction of the base cations stored in soils are bound in mineral structures and are unavailable to plants. The pool of dissolved base cations resides in the soil as cations that are adsorbed to negatively-charged exchange sites. They can become desorbed in exchange for hydrogen or

aluminum, and are thus termed exchangeable cations. The process of weathering gradually breaks down rocks and minerals, returning their stored base cations to the soil in dissolved form and thereby contributing to the pool of adsorbed base cations. Base cation reserves are gradually leached from the soils in drainage water, but are constantly being resupplied through weathering and deposition. It is well known, however, that elevated leaching of base cations by acidic deposition might deplete the soil of exchangeable bases faster than they are resupplied via weathering and base cation deposition (Cowling and Dochinger 1980).

Likens et al. (1996) concluded that acidic deposition enhanced the release of base cations from forest soils at the Hubbard Brook Experimental Forest in New Hampshire (HBEF) from the mid-1950s until the early 1970s, but that, as the labile pool of base cations in soil became depleted, the concentrations in streamwater decreased from 1970 through 1994 by about one-third. The marked decrease in base cation deposition inputs and concomitant increase in net soil release of base cations at HBEF have likely depleted soil pools to the point where ecosystem recovery from decreased S deposition will be seriously delayed. Moreover, Likens et al. (1996) suggested that recently observed declines in forest biomass accumulation at HBEF might be attributable to Ca^{2+} limitation or Al-toxicity, which can be expressed by the Ca:Al ratio in soil solution (Cronan and Grigal 1995).

3.3.2.2. Evidence for Nitrogen Saturation in Forests

Nitrogen is an essential nutrient for both aquatic and terrestrial organisms, and is a growth-limiting nutrient in most terrestrial temperate zone ecosystems. Thus, N inputs to natural systems are not necessarily harmful. For each ecosystem, there is an optimum N level which will maximize ecosystem productivity without causing significant changes in species distribution or abundance. Above the optimum level, harmful effects can occur in both aquatic and terrestrial ecosystems (Gunderson 1992, Aber et al. 1998).

The N cycle is extremely complex and controlled by many factors besides atmospheric emissions and deposition (Aber et al. 1991, 1998). Increased atmospheric deposition of N does not necessarily cause adverse environmental impacts. Nitrogen inputs that may be beneficial to some species or ecosystems may be harmful to others. In most areas, added N is taken up by terrestrial biota and the most visible effect seems to be an increase in forest productivity (Kauppi et al. 1992). However, under certain circumstances, atmospherically-deposited N can exceed the capacity of forest ecosystems to take up N. In some areas, especially at high elevation, terrestrial

ecosystems have become N-saturated[2] and high levels of deposition have caused elevated levels of NO_3^- in drainage waters (Aber et al. 1989, 1991; Stoddard 1994). This enhanced leaching of NO_3^- causes depletion of Ca^{2+} and other base cations from forest soils and can cause acidification of soils and drainage waters in areas of base-poor soils.

Analyses have been conducted in the northeastern United States and Europe to examine the relationships between N deposition and NO_3^- leaching to surface waters. The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet-inputs greater than approximately 400 eq/ha/yr (5.6 kg N/ha/yr). Stoddard (1994) presented a geographical analysis of patterns of watershed loss of N throughout the northeastern United States. He identified approximately 100 surface water sites in the region with sufficiently intensive data to determine their N status. Sites were coded according to their presumed stage of N retention, and sites ranged from Stage 0 (background condition) through Stage 2 (chronic impacts). The geographic pattern in watershed N retention depicted by Stoddard (1994) followed the geographic pattern of N deposition. Sites in the Adirondack and Catskill Mountains in New York, where N deposition was about 11 to 13 kg N/ha/yr, were typically identified as Stage 1 (episodic impacts) or Stage 2. Sites in Maine, where N deposition was about half as high, were nearly all Stage 0. Sites in New Hampshire and Vermont, which received intermediate levels of N deposition, were identified as primarily Stage 0, with some Stage 1 sites. Based on this analysis, a reasonable threshold of N deposition for transforming a northeastern site from the "natural" Stage 0 condition to Stage 1 would correspond to the deposition levels found throughout New Hampshire and Vermont, approximately 8 kg N/ha/yr. This agreed with Driscoll et al.'s (1989) interpretation, which suggested N leaching at wet inputs above about 5.6 kg N/ha/yr that would likely correspond to total N inputs near 10 kg N/ha/yr because total deposition is often nearly double the wet deposition amount. This is likely the approximate level at which episodic aquatic effects of N deposition would become apparent in many watersheds of the eastern United States.

Analysis of data from surveys of N outputs from 65 forested plots and catchments throughout Europe were conducted by Dise and Wright (1995) and Tietema and Beier (1995). Below the throughfall inputs of about 10 kg N/ha/yr, there was very little N leaching at any of

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[2] The term N-saturation has been defined in a variety of ways, all reflecting a condition whereby the input of N (e.g., as NO_3^-, ammonium) to the ecosystem exceeds the requirements of terrestrial biota and a substantial fraction of the incoming N leaches out of the ecosystem as NO_3^- in groundwater and surface water.

the study sites. At throughfall inputs greater than 25 kg N/ha/yr, the study catchments consistently leached high concentrations of inorganic N. At intermediate deposition values (10-25 kg N/ha/yr), Dise and Wright (1995) observed a broad range of watershed responses. Nitrogen output was most highly correlated with input N (r^2=0.69), but also significantly correlated with input S, soil pH, percent slope, bedrock type, and latitude. A combination of input N (positive correlation) and soil pH (negative correlation) explained 87% of the variation in output N at 20 sites (Dise and Wright 1995).

Nitrate leaching losses from soils to drainage waters are governed by a complex suite of ecosystem processes in addition to N inputs from atmospheric deposition. In particular, mineralization and nitrification processes play important roles in regulating the quantity of, and temporal variability in, the concentration of NO_3^- in soil solution, and consequently leaching losses from the rooting zone (Johnson et al. 1991a,b; Joslin et al. 1987; Reuss and Johnson 1986). Thus, NO_3^- leaching is mostly under biological control and typically shows pronounced seasonal variability (Van Miegroet et al. 1993). Peak concentrations of NO_3^- in soil solution appear to be largely responsible for the potentially toxic peaks in aluminum concentration that sometimes occur in soil solution, although SO_4^{2-} may also play a role by serving to elevate chronic Al concentrations (Eagar et al. 1996).

High leaching of NO_3^- in soil water and streamwater draining high-elevation spruce-fir forests has been documented in numerous studies in the Southern Appalachian Mountain (SA) region (c.f., Joslin and Wolfe 1992; Joslin et al. 1992; Van Miegroet et al. 1992a,b; Nodvin et al. 1995). This high NO_3^- leaching has been attributed to a combination of high N deposition, low N uptake by forest vegetation, and inherently high N release from soils. Forest age is another major factor affecting uptake, with mature forests requiring minimal N for new growth and, hence, often exhibiting higher NO_3^- leaching that younger, more vigorous stands (Goodale and Aber 2001). Old-growth red spruce stands in the SA have been demonstrated to have significantly slower growth rates than stands younger than 120 years (Smith and Nicholas 1999). The latter feature is associated with low carbon to N ratios in mineral soil, high N mineralization potential, and high nitrification (Joslin et al. 1992, Eagar et al. 1996).

In general, deciduous forest stands in the eastern U.S. have not progressed toward N-saturation as rapidly or as far as spruce-fir stands, in part because they tend to be located at lower elevations and receive lower atmospheric inputs of N. Many deciduous forests have higher rates of N uptake and requirement than spruce-fir forests. Decreased growth and increased mortality

have more commonly been observed in high-elevation coniferous stands than in lower elevation hardwood forests, and have been attributed by some to excess inputs of N (Aber et al. 1998). Indeed, many of the lower elevation deciduous stands are N-deficient and are therefore likely to benefit (i.e., grow faster), at least up to a point, with increased inputs of N.

There are examples of N saturation in lower-elevation eastern forests, especially in West Virginia. For example, progressive increases in streamwater NO_3^- and Ca^{2+} concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s (Edwards and Helvey 1991; Peterjohn et al. 1996; Adams et al. 1997, 2000). This watershed has received higher N deposition (average throughfall input of 22 kg/ha/yr of N deposition in the 1980s) than is typical for low-elevation areas of the eastern United States, however (Eagar et al. 1996), and this may explain the observed N saturation.

3.3.3. Flora

3.3.3.1. Lichens

Lichens are frequently used as indicators of air pollution and atmospheric deposition levels. In addition to being good subjects for biomonitoring, they constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser 1997, Brodo et al. 2001). There are several potential uses of lichens for air pollution and deposition monitoring (Blett et al. 2003):

- measurement of tissue concentrations of specific pollutants (e.g., S, N, Hg, other heavy metals) within lichen species that are not sensitive to adverse health impacts from these pollutants (i.e., use lichens as passive monitors of pollution);
- determination of changes in species composition or the presence/absence of sensitive species (i.e., evaluate adverse impacts of pollutants on lichen distribution and abundance);
- identification of areas having relatively high levels of air pollution, where monitoring instrumentation should be installed to more quantitatively measure pollution levels.

Epiphytic macro lichens (those that grow attached to trees or other plants) are generally the best indicators of air pollution. Their tissue content of contaminants is generally reflective of the amount of ambient atmospheric pollution. Individual species exhibit different sensitivities to atmospheric pollutants, with some species being adversely impacted at air pollution levels that may not be considered high relative to other AQRVs. Particularly sensitive genera include

Alectoria, *Bryoria*, *Ramalina*, *Lobaria*, *Pseudocyphellaria*, *Nephroma*, and *Usnea* (McCune and Geiser 1997, Blett et al. 2003, www.nacse.org/lichenair).

Assessment of long-term change in the epiphytic lichen community can be especially valuable to provide an early indication of either improving or deteriorating air quality and atmospheric deposition (Blett et al. 2003). Such monitoring was incorporated in 1994 into the U.S. Forest Service Forest Inventory and Analysis (FIA) Program (see http://fia.fs.fed.us/lichen).

3.3.3.2. Vascular Plants

Concerns have been cited since the early 1970s about potential forest declines that could result from soil acidification and nutrient deficiency brought about by acidic deposition. In addition, concerns have arisen regarding the mobilization of Al in forest soils due to inputs of acidic deposition, and the potential toxicity of that Al to forest stands (Cronan and Grigal 1995).

Acidic deposition has contributed to a decline in the availability of Ca^{2+} and other base cations in the soils of acid-sensitive forest ecosystems by the leaching of base cations from foliage and from the primary rooting zone and by the mobilization of Al from soils to soil solution and drainage water (Eager and Adams 1992, NAPAP 1998). Both N and S deposition have contributed to these mechanisms. Foliar Ca^{2+} levels and soil and root Ca:Al ratios are considered low to deficient over large portions of the spruce-fir region in the eastern United States (Joslin et al. 1992, Cronan and Grigal 1995, NAPAP 1998). Aluminum mobilization from already acid soils can also impede Ca^{2+} and magnesium uptake and potentially induce plant deficiencies in these nutrients.

Forest resources that are potentially sensitive to the adverse impacts of acidic deposition are found throughout the United States, in particular at higher elevation sites. However, NAPAP (1998) concluded that the only cases of significant forest damage in the United States for which there was strong scientific evidence at that time that acidic deposition was a primary cause included the observed reduced growth of red spruce in the SA and increased mortality and decline of red spruce in the Northeast. Spruce-fir forests are generally found at relatively high elevation, for example above 1,400 m in the SA (SAMAB 1996).

High-elevation areas are often dominated by relatively unreactive bedrock, and base cation production via weathering is limited (Elwood et al. 1991). Soils in such areas tend to have thick organic horizons, high organic matter content in the mineral horizons, and low pH (Joslin et al. 1992). Because of the largely unreactive bedrock, base-poor litter and organic acid anions

produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these high-elevation forests often tends to be below about 10% and the soil cation exchange complex is generally dominated by Al (Johnson and Fernandez 1992, Joslin et al. 1992).

Results of the NuCM modeling exercises conducted by Sullivan et al. (2002), together with the results of NuCM simulations published for other watersheds in the SA region, suggest that spruce-fir forests in the region are likely to experience decreased Ca:Al ratios in soil solution under virtually all strategies of future acidic deposition considered. This is partly because S adsorption in soils is likely to decline, even with dramatically reduced S deposition. In addition, many spruce-fir forests in the region are N-saturated, and continued N deposition at moderate or high levels would be expected to contribute to elevated NO_3^- concentrations in soil water, which could further enhance base cation leaching and mobilization of Al from soils to soil solution. These processes will be facilitated by the already low values of base saturation in the soils of many of these forests. Results of modeling efforts conducted to date are consistent in suggesting that such changes to forest soils and soil solutions will likely continue to occur.

It is not clear, however, to what extent these changes in the chemistry of soils and soil solutions might actually impact forest growth and health. The state of scientific understanding on this topic would suggest that such chemical changes would increase the likelihood that the growth and/or health of spruce-fir forests would be adversely impacted, perhaps making them more susceptible to other stressors associated with such factors as insect pests, pathogens, or extreme climatic conditions. However, the occurrence of low base saturation and Ca:Al ratio in soil solution will not necessarily be sufficient to cause widespread impacts. Many factors in addition to soil base saturation and soil solution acid-base chemistry are important in this regard. Recent evidence indicates that mortality in red spruce in the SA region is not abnormal when compared to historical rates, and that Fraser fir stands killed by the balsam wooly adelgid are largely being replaced by vigorous re-growth of young stands of that species. To what extent spruce or fir mortality will be replaced with a species mix similar to that existing prior to the mortality remains to be seen.

The limited available empirical data suggest that the kinds of changes in soil solution chemistry projected by NuCM for spruce-fir stands in the SA region will be consistent with the kinds of changes that have been associated in the past with reductions in forest growth. The weight of evidence for spruce-fir forests suggests that adverse impacts on soil solution chemistry are likely, and adverse impacts on forest growth and health are possible. Changes in red spruce

growth rates are potentially attributable, at least in part, to base cation deficiencies caused by inhibition of base cation uptake by trees due to elevated Al concentration in soil solution within the rooting zone. Other factors that could also be important include depletion of base cations in upper soil horizons by acidic deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidic deposition, especially cloud deposition.

The state of scientific understanding is less clear with respect to the lower elevation hardwood forests. Available information is not sufficient to draw conclusions regarding the increased likelihood of future effects on the condition of hardwood forests in the SA region (Sullivan et al. 2002). Certainly, such effects are less likely for hardwood forests than for spruce-fir forests.

Forest trees are not the only vascular plants that are potentially sensitive to acidic deposition. Available data suggest that some tree species can be sensitive to base cation depletion and/or Al toxicity, and it is possible, or perhaps likely, that a variety of shrubs and herbaceous species are similarly sensitive. Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in response to acidic deposition. Data are insufficient in this country, however, to allow us to use shrub or herbaceous plant species as indicators of the effects of acidic deposition at this time.

The possible effects of acidic deposition on wetland, riparian, meadow, and alpine plant communities are also of significant concern. Especially important in this regard is the role of N deposition in regulating ecosystem N supply and plant species composition. Key concerns are for listed threatened or endangered species and species diversity. However, for most rare, threatened, or endangered herbaceous plant species, little is known about their relative sensitivities to atmospheric deposition inputs. Although species diversity is highly valued, it can be difficult and expensive to document changes in this parameter in response to atmospheric deposition. For these reasons, we do not advocate inclusion of wetland, riparian, meadow, or alpine plant communities in the Forest Service national programs for AQRV monitoring and research.

Forest health is an elusive concept. It can be reflected by a variety of physiological indicators, including, for example, changes in the growth rate of trees, foliar damage, susceptibility to insects or disease, and tree mortality. Similarly, forest health can be affected by a host of potential stressors, of which air pollution is only one possibility. Climate, stand competition, outbreak of non-native pathogens, and forest management (alone or in combination)

often contribute greatly to observed forest health problems. Attempts to document, and in particular to quantify, the effects of air pollution on forest health have encountered considerable complexity and uncertainty. Nevertheless, such efforts have produced some evidence that suggests that red spruce, and perhaps also sugar maple, in some areas have experienced declining health as a consequence of acidic deposition. Available evidence for the SA was reviewed by Eagar et al. (1996) and is summarized in Appendix C.

It is important to note that, at most forested locations in the United States, it is unlikely that terrestrial effects of atmospheric deposition can be documented by conducting vegetation studies. This is because levels of atmospheric deposition of S and N are usually below expected damage thresholds for most tree species, assessment of forest health is extremely complex, and trees typically respond to a wide variety of stressors in addition to atmospheric deposition. It is therefore more likely that the results of vegetative studies will be useful as corroborating evidence, to be used in conjunction with results of analysis of soil and/or drainage water chemistry when assessing AQRVs.

When vegetation analyses are conducted as part of Air Program studies, it might be helpful to use protocols that are already in place within existing Forest Service inventory and monitoring programs. Forest Inventory Analysis field methods for vegetation diversity and structure were derived from the Forest Health Monitoring Program. They specify measurements of species composition and relative abundance and vertical position of trees, shrubs, herbs, grasses, and ferns within study plots. Nested plots of different sizes are used within a given plant community to determine characteristics of tree, shrub, and herbaceous species (c.f., Mueller-Dombois and Ellenberg 1974, Barbour et al. 1987). This survey information is used to assess forest ecosystem health by documenting diversity and rates of change in community structure. Changes in the composition or spatial arrangement of forest plants can illustrate the influence of chronic stress, such as from air pollution or climate change. Such stresses can reduce or eliminate sensitive species and also can lead to the dominance of opportunistic species, including many non-native weedy species. Data on vegetative diversity and structure can also be used to classify stands by community type. This facilitates intercomparison of data from multiple plots. Details on FIA field techniques are found in the FIA website (www.fia.fs.fed.us).

3.4. Recommended Assessment Approaches

There are many approaches that can be used by the Forest Service to assess 1) the sensitivity of aquatic and terrestrial natural resources to potential degradation from atmospheric deposition of S, N, or toxic materials, and 2) the extent to which sensitive aquatic or terrestrial natural resources have been harmed in the past or might be expected to be harmed in the future under assumed scenarios of air pollution and atmospheric deposition. It is beyond the scope of this report to attempt to review all of those approaches. Rather, in this section of the report, we attempt to highlight a number of approaches that can be broadly useful to the Forest Service across the United States. We recommend that such approaches be routinely considered in making evaluations regarding atmospheric deposition sensitivity and/or effects. It must be recognized that there are many additional approaches that might be considered to also be appropriate in particular regions or situations. Our failure to discuss a certain approach should not be taken as an indication that the approach in question is not valuable.

3.4.1. Chemical Criteria

Sensitivity of surface waters to chronic and episodic acidification is not solely a function of surface water ANC, but depends also upon watershed soils, mineralogy, and hydrologic flow paths (Chen et al. 1984, Cosby et al. 1985), as well as on the current and historic atmospheric depositional loadings of acids and bases. Nevertheless, surface water ANC provides an initial point of departure from which to assess quantitatively the current status of streams on a synoptic scale. Baker et al. (1990a) used ANC cutoffs of 0, 50 and 200 μeq/L for reporting on national lake and stream population estimates. ANC ≤ 0 μeq/L is of significance because waters at or below this level have no capacity to neutralize acid inputs; they are acidic by definition. Surface waters with ANC ≤ 50 μeq/L have been termed "extremely acid sensitive" (Schindler 1988), are prone to episodic acidification in some regions (DeWalle et al. 1987, Eshleman 1988), and may be susceptible to future chronic acidification at current or increased rates of acidic deposition.

Common reference values for pH are 5.0, 5.5, and 6.0. Such values are often used to evaluate the possible extent of adverse effects on fish and other aquatic organisms. Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Haines and Baker 1986, Baker et al. 1990c). The effects of low pH are specific to the organism and region under consideration and depend also upon the concentrations of other chemical constituents in the water, notably Al_i and Ca^{2+}. Lakes or streams having pH below about 5.0 or

ANC below about 0 generally do not support fish. Depending on the region, waters having pH above about 6.5 and ANC above about 50 μeq/L support large, but variable, numbers of species. Populations of salmonid fish are generally not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.2 to 5.5 (Haines and Baker 1986). A number of synoptic surveys indicate loss of species diversity and absence of many other fish species at a pH range of 5.0 to 5.5 (Haines and Baker 1986). Levels of pH less than 6.0 to 6.5 have been associated with adverse effects on populations of dace, minnows, and shiners (family Cyprinidae), and bioassays suggest that given sufficient Al concentrations, pH less than 6.5 can lead to increased egg and larval mortality in blueback herring (*Alosa aestivalis*) and striped bass (*Morone saxatilis*) (Klauda et al 1987; Hall 1987).

Aluminum toxicity to aquatic organisms is thought to be caused primarily by Al_i rather than organically complexed Al (Driscoll et al. 1980, Baker and Schofield 1982, Havas 1985). There is limited evidence of biological effects at Al_i less than 50 μg/L. Free Al concentrations (roughly equivalent to Al_i concentrations at low pH values) between 50 and 200 μg/L have been demonstrated to reduce the growth and survival of various species of fish (Muniz and Leivestadt 1980, Baker and Schofield 1982). Concentrations of Al_i greater than 200 μg/L are generally considered to have toxic effects on the majority of freshwater fish species.

The U.S. EPA is in the process of attempting to set nutrient criteria for total N and P concentrations in U.S. lakes (U.S. EPA 2000a), and streams and rivers (U.S. EPA 2000b). Different nutrient criteria are being developed for each of 14 different nutrient ecoregions throughout the country. Nutrient ecoregions are based on aggregations of level III Omernik ecoregions. Draft nutrient guidelines are available on the web (http://www.epa.gov/waterscience/criteria/nutrient/ecoregions/sumtable.pdf).

3.4.2. Chemical Ratios

Ion ratios can be used to evaluate water chemistry and to infer something about the various possible causes of water quality degradation. Ratios that reflect the inter-relationships among SO_4^{2-}, SBC, and ANC are commonly used as a means of providing a qualitative assessment of chemical change. In particular, the ratio $[SO_4^{2-}]/[SBC]$ quantifies the SO_4^{2-} concentration relative to surface water susceptibility to acidification (Husar et al. 1991).

Herlihy et al. (1991) used ratios of organic and inorganic acid anions to determine probable source of acidity in surface water survey data. Sites with organic anion concentrations

greater than SO_4^{2-} + NO_3^- concentrations were determined to be organic-dominated and likely acidic due to naturally occurring organic acids. Sites where organic anions were less than 10% of the total acid anions were classified as inorganic-dominated. Any site with SO_4^{2-} concentrations more than twice that expected from atmospheric S deposition was classified as a watershed SO_4^{2-} source (e.g. acid mine drainage). The surface water N:P molar ratio is also used to assess whether waters are N or P limited. Waters with N:P greater than 16 are generally considered P limited, while those below 16 are N limited.

3.4.3. Taxonomic Richness

Taxonomic richness is a metric that is commonly used to quantify the impacts of an environmental stress, such as acidification or eutrophication. The richness metric can be applied at various taxonomic levels. For example, the number of fish species can be used as an index of acidification (c.f., Bulger et al. 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera; Sullivan et al. 2003).

Different stressors have different effects on aquatic taxa richness and community composition. Both acidification and the effects of pesticides and other toxics affect the most sensitive species first. For these stressors, loss of sensitive species and decreased richness are indicators of increased disturbance. Eutrophication is more complicated. Adding nutrients to a low nutrient (oligotrophic) aquatic system often causes an increase in taxonomic richness if nutrient additions are moderate. Large additions of nutrients, however, often result in decreased taxonomic richness. Both total taxa richness and specific sensitive taxa presence/absence may be used as indicators of condition and response to stress. Sensitive taxa lists must be tailored to the specific stressor and study area of interest.

3.4.4. Community Composition and Sensitive Species

It is often useful to document overall aquatic community composition (list of species names and their relative abundance). Karr (1981) first introduced the concept of a multimetric index of biotic integrity (IBI) that was based on fish assemblages. Similar indices have been developed for benthic macroinvertebrates and periphyton. The rationale behind such indices is that a set of variables, or metrics representing community structure (taxa richness, relative abundance, dominance), pollution tolerance, functional feeding groups and habitat behavioral responses, life history strategies, disease, and density offers robust and sensitive insights into

how an assemblage responds to natural and anthropogenic stressors. Another approach in use for aquatic community composition assessment is the predictive modeling approach called River Invertebrate Prediction and Classification System (RIVPACS). Variations of this approach have been used extensively in both Australia and the United States (Hawkins et al. 2000). In this method, reference (good condition) sites are modeled to develop lists of taxa expected to be found at good sites relative to site environmental characteristics. Lists of observed (O) taxa at study sites are compared to the modeled expected (E) lists and the ratio of observed/expected (O/E) taxa calculated. O/E scores around 1 indicate a site that has taxa indicative of good condition. O/E scores near zero indicate a site with little resemblance to reference condition.

3.4.5. Forest Growth and Health

3.4.5.1. FHM/FIA Approaches for Assessment of Tree Growth and Health

It is likely that any studies of forest growth and/or health to be conducted in conjunction with the Forest Service Air Program will follow protocols and procedures of the Forest Health Monitoring Program (FHM), which is now part of the FIA project. FHM/FIA protocols include tree growth and damage assessment. Tree diameter is measured at breast height and/or at the root collar. Procedures are specified to allow remeasurement at the same location in subsequent years. Damage is characterized according to three attributes: location, type, and severity of damage. Damage signs are prioritized based on location. Stocking and regeneration data are collected by counting live seedlings on microplots, by condition class. Data are collected from at least one site tree for each accessible forest land condition class. The site tree is selected from among those that have remained in a dominant or co-dominant canopy position throughout their life span, and that have not been visibly damaged or suppressed.

3.4.5.2. Indices of Acidic Deposition Impacts

Cronan and Grigal (1995) proposed that a molar ratio of Ca:Al concentration equal to 1.0 in soil water be used as a general index, suggesting an increasing probability of stress to forest ecosystems. It cannot be interpreted as a single cutoff point, and variability is high. Tree species vary widely in their sensitivity to Al stress. In addition, Al concentrations in soil solution often exhibit pronounced spatial and temporal variability. Finally, the form of Al present in solution plays an important role in determining toxicity. For example, organically-complexed Al, which predominates in upper, organic-rich soil horizons, is essentially nontoxic.

The Ca:Al molar ratio of 1.0 may be interpreted as an index of warning that an ecosystem might be entering a zone of increased stress. However, many tree species may not exhibit obvious symptoms of stress until this ratio reaches levels substantially lower than 1.0. Conversely, tree roots exposed to a ratio higher than 1.0 may experience mild chronic stress without exhibiting above-ground symptoms.

A variety of factors predispose soils of high-elevation spruce-fir forests to potential Al toxicity and Al-induced inhibition of cation uptake. These factors include features of the climate (high precipitation, low temperature), vegetation (coniferous litter), bedrock (low base cation production), and soil forming processes such as podzolization (Eagar et al. 1996). Because base saturation in spruce-fir forests in the eastern United States tends to be very low, continued input of NO_3^- and/or SO_4^{2-} from atmospheric deposition might further acidify the soils and/or contribute to further Al mobilization from soils to soil solution (Johnson and Fernandez 1992). Increased mineral acid anion concentrations (NO_3^-, SO_4^{2-}) in soil will cause the mobilization of Al ions from the exchange sites of acid soils. Although base cations normally dominate exchange sites in the soil compared to Al, base cation reserves are so low in acidic soils that Al exchange dominates. Dissolved Al concentrations in soil solution at spruce-fir study sites frequently exceed 50 µM and sometimes exceed 100 µM (Joslin and Wolfe 1992, Johnson et al. 1991b, Eagar et al. 1996). All studies reviewed by Eagar et al. (1996) showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution. They speculated that the occurrence of periodic large pulses of NO_3^- in solution were important in determining Al chemistry.

3.4.6. Critical Load

Consideration of acid deposition standards or critical loads for the protection of surface water quality from potential adverse effects of S and N deposition is a multifaceted problem. Some approaches require that S and N be treated separately as potentially-acidifying agents. Appropriate criteria must be selected as being indicative of damaged water or soil chemistry, for example ANC, NO_3^- concentration, pH, or base saturation. Once a criterion has been selected, a critical value must be estimated, above or below which the criterion should not be permitted to rise or fall. Selection of a critical value for ANC or pH is confounded by the existence of lakes and streams that are low in pH or ANC due entirely to natural factors, irrespective of acidic deposition. In particular, low concentrations of base cations in solution, due to low weathering

rates and/or minimal contact between drainage waters and mineral soils, and high concentrations of organic acids contribute to naturally low pH and ANC in some surface waters (Sullivan et al. 2005).

Acid deposition standards might be selected on the basis of protecting aquatic systems from chronic acidification; conversely, episodic acidification might also be considered, and would be of obvious importance in regions where hydrology is dominated by spring snowmelt. Episodic acidification is considered to be biologically-relevant for high-elevation aquatic ecosystems (e.g., Barmuta et al. 1990, Kratz et al. 1994). Some high-elevation aquatic ecosystems are also sensitive to fertilization, as well as acidification, effects of N deposition. Thus, selection of appropriate acid deposition standards involves consideration of a matrix of factors.

A target load (c.f., Henriksen and Brakke 1988) can be based on political, economic, or temporal considerations, and may imply that the environment will be protected to a specified level (i.e., certain degree of allowable damage) and/or over a specified period of time. There has been a rapid acceptance of the concepts of critical and target loads throughout Europe and in Canada for use in political negotiations concerning air pollution and development of abatement strategies to mitigate environmental damage (e.g., Posch et al. 1997).

Criteria of unacceptable change used in critical loads assessments are typically set in relation to known or expected effects on aquatic or terrestrial organisms. For protection of aquatic organisms, the ANC of runoff water is most commonly used (Nilsson and Grennfelt 1988, Henriksen and Brakke 1988, Sverdrup et al. 1990). Concentrations, below which ANC should not be permitted to fall, have been set at 0, 20, and 50 μeq/L for various applications (e.g., Kämäri et al. 1992).

Clearly, the selection of appropriate targets and associated critical loads strongly influence interpretation of the critical load model output for any watershed. The goal of the Prevention of Significant Deterioration (PSD) process is to protect sensitive resources from adverse impacts. Unfortunately, the lower limit of acid-base chemical change (e.g., in ANC) that would elicit a biological response in acid-sensitive streams or lakes is not well known. Various species of fish have been shown to respond to lowered pH or ANC by exhibiting higher mortality, particularly at pH levels near 5.0, which roughly correspond with ANC=0. Experimental depressions in pH and ANC, equivalent to spring snowmelt pulses, have been

shown to affect high-elevation stream invertebrate populations (Kratz et al. 1994) and lake zooplankton (Barmuta et al. 1990).

The sensitivities of brook trout and several other fish species that commonly occur in the eastern United States to acidification are well known. In the Adirondack Mountains of New York, about half of the 52 fish species recorded in the Adirondack Lakes Survey (Kretser et al. 1989) did not occur in lakes having pH less than 6 (Driscoll et al. 2003). Such lakes have ANC below about 30 μeq/L (Munson et al. 1990). A pH = 6 threshold has been cited as a recovery goal for acidified lakes in eastern Canada (Holt and Yan 2003) and ANC = 20 for an acidified river in Norway (Raddum and Fjellheim 2003).

It has also been shown that native western trout are sensitive to short-term increases in acidity. For example, Woodward et al. (1989) exposed native western cutthroat trout to pH depressions (pH 4.5 to 6.5) in the laboratory. Reductions in pH from 6.5 to 6.0 in low-Ca^{2+} water (70 μeq/L) did not affect survival, but did reduce growth of swim-up larvae. Eggs, alevins, and swim-up larvae showed significantly higher mortality at pH 4.5 as compared to pH 6.5. Mortality was also somewhat higher at pH 5.0, but only statistically higher for eggs. Some species of aquatic biota in western aquatic ecosystems have been shown to be somewhat more sensitive to pH and ANC change than are cutthroat trout (Baker et al. 1990c).

A critical load threshold of ANC = 0 might be selected as a threshold below which chronic chemical changes are likely to affect native fish populations. ANC thresholds of 20 and 50 μeq/L provide a margin of error to allow for episodic ANC depressions during snowmelt or rainfall events. Some species of aquatic biota in western lakes and streams are probably sensitive to ANC depression to values below 20 μeq/L, although it is less certain that ANC changes at or below 50 μeq/L result in direct biological effects in high-elevation western systems (e.g., Barmuta et al. 1990).

Selection of the best, or most appropriate, criterion and target load for protecting aquatic resources is not a scientific issue. It is a policy issue that must be addressed by resource managers, based in part on the best available scientific information. FLMs may want to protect the sensitive resource against biological changes that are difficult or impossible to measure or to attribute to atmospheric deposition. Simulations from watershed models can provide useful information to be used in the decision process. However, the final determination must be based on policy judgment, not science (Sullivan et al. 2005).

3.5. Confounding Factors

3.5.1. Inherent Sensitivity

In most regions of the United States, the majority of lakes, streams, and forest stands are not highly sensitive to existing levels of ambient air pollution. In addition, air pollution levels are generally decreasing in many parts of the country, especially in the eastern United States, in response to federal and state air pollution control regulations. Therefore, the highly sensitive, and impacted, systems tend to be restricted to a relatively small percentage of the overall aquatic and/or terrestrial resource base. There are exceptions to this generalization such as, for example, in Monongahela National Forest, West Virginia, where a high percentage of the streams are acid-sensitive and acid-impacted (c.f., Sullivan and Cosby 2004). Nevertheless, in most cases, it is important to focus research or monitoring efforts on the relatively small subset of the overall resource that is most sensitive or that has been most affected by air pollution. This fact has important implications for study site selection. Depending on the objectives of the particular study, it may be necessary to devote substantial effort to site selection in order to ensure that sampling is conducted in ecosystems that are most sensitive to air pollution degradation. It may be difficult to quantify effects on ecosystems that are only moderately sensitive. In addition, it is important for FLMs to monitor conditions within the most sensitive ecosystem elements and attempt to rectify documented or suspected adverse impacts.

3.5.2. Hydrological Flow Paths

The effects of acidic deposition on lakes and streams are strongly controlled by the flowpath of water through the terrestrial watershed. Hydrology is an important controlling factor for deposition impacts in all settings (Turner et al. 1990), but hydrology is of particular importance in alpine and subalpine ecosystems. The depth and chemical composition of soils, talus, and colluvium and the slope of the watershed collectively determine the residence time of subsurface water within the watershed, extent to which snowmelt and rainfall runoff interact with soils and geologic materials, and consequently the extent of NO_3^- uptake by biota versus NO_3^- leaching and acid neutralization within the watershed (Sullivan 2000).

Streamflow at the beginning of the melt period in high-elevation areas often has a large component of "old water" (water stored in soils and talus over winter) that was displaced into the stream by the piston effect as meltwater infiltrated the soil and talus areas. After the pre-event soil waters have been flushed into streams, streamflow is generated to a larger extent by

snowmelt, with increasing amounts of surface flow during the main melting event. During the initial stages of snowmelt, therefore, stream chemistry reflects the months of weathering and decomposition products that accumulated in soils and talus areas under the snowpack and were pushed into streams by the piston effect. As the melt continues, the contribution of pre-event water declines and the composition of streamwater is increasingly controlled by relatively rapid geochemical reactions between soils and talus and the infiltrating snowmelt (Mast et al. 1995).

3.5.3. Land Use

Landscape processes and watershed disturbance can influence soil and water acidification. Land use practices and vegetation patterns have changed in various parts of the United States for decades to centuries. These changes in human activity can influence the response of forested ecosystems to external stressors, including atmospheric deposition of S or N, natural disturbance factors such as wind and fire, and climatic changes. Some processes contribute to the acidification of soil and surface waters or reduce the base saturation of the soils thereby increasing their sensitivity to acidic deposition. Other processes cause decreased acidity (Sullivan et al. 1996b, Sullivan 2000).

Watershed disturbance from logging, blowdown, and fire disrupts the normal flow of water and can cause increased contact between runoff water and soil surfaces, leading to increased base cation concentration and ANC in drainage water. Recovery from disturbance can cause a decrease in drainage water ANC as the system returns to pre-disturbance conditions. In particular, soil loss through erosion can reduce the base cation pool size, thereby limiting the capacity of soils to neutralize atmospheric acidity. In addition, forest harvesting has an important effect on forest N-demand, thereby reducing the likelihood of future N-saturation in response to high N deposition. Forest management practices, especially those that have occurred over many generations, have had important effects on soil, nutrient supplies, and organic material.

Forests are efficient at removing S and N from the atmosphere. Forest canopy, particularly differences between deciduous and coniferous stands, can influence rates of dry deposition of S and N. In high-deposition regions, forests exacerbate acidification by increasing total deposition. In some cases, dry and occult deposition can contribute more S to a forest ecosystem than wet deposition (Rustad et al. 1995). Also, there are differences in nutrient uptake

among trees of different age classes, with younger stands taking up larger quantities of N and other nutrients as compared with older stands.

Removal of the forest affects drainage water quality several ways. Deposition of S and N are reduced. Leaching of NO_3^- increases and in some cases causes a pulse of surface water acidification. Base cations are lost. Regrowth of the forest may further affect drainage water quality through vegetation uptake of N and base cations. Trees accumulate base cations to a greater degree than anions. In order to balance the charge discrepancy, roots release an equivalent amount of protons and acidify the soil. Base cation accumulation by trees is age-dependent. Young forests grow faster and are therefore more acidifying than older forests (Nilsson et al. 1982, Nilsson 1993). They also retain greater amounts of N.

3.5.4. Climate

Climate can influence watershed acid sensitivity and the effects of acidic deposition and eutrophication. Drought alters hydrologic flowpaths and changes the relative contribution of near-surface runoff versus deeper baseflow. Because these source areas typically generate different levels of ANC, such changes in hydrologic input can influence surface water acid-base chemistry (Webster et al. 1993, Newell 1993, Sullivan 2000). The amount of precipitation, especially during winter, has been shown to affect the total annual wet deposition of S and N. Also, a large proportion of the snowpack deposition load is released during the early phases of snowmelt. Watersheds that receive snow are exposed to greater episodic acidification during years with greater precipitation.

Drought conditions were judged by Melack et al. (1998) to be responsible for increasing the proportion of runoff derived from shallow groundwater in the Ruby Lake basin in the Sierra Nevada, as evidenced by an increase in SO_4^{2-} concentration from about 6 to 12 μeq/L during the period 1987 through 1994. Melack et al. (1998) also speculated that drought could be responsible for increases in N retention in the Emerald Lake catchment. The monitoring data illustrated a 25% to 50% reduction in annual NO_3^- maxima and minima in Emerald Lake, with a concomitant shift in the lake phytoplankton community from P-limitation towards N-limitation (Melack et al. 1998).

Temperature can influence the response of surface waters to acidic deposition via effects on the timing and magnitude of snowmelt, frequency and magnitude of episodic acidification, and influence on other watershed processes. Under cool, moist conditions, atmospheric S inputs

can be stored as reduced S in soils, especially in wetland areas. This storage protects surface waters from acidification (Rochefort et al. 1990). However, under warmer and drier climatic conditions, this stored S can be reoxidized and consequently released to drainage waters during periods of rainfall or snowmelt (Bayley et al. 1992, LaZerte 1993, Schindler 1998). Temperature can also have a variety of effects on S and N dynamics and has a large influence on biological uptake of N within both terrestrial and aquatic ecosystems.

3.5.5. Insect Infestation

Forest insect infestation can have profound effects on the acid-base and nutrient chemistry of soils and drainage waters. Effects of a gypsy moth infestation in Shenandoah National Park (SHEN) provide a good example. Between the mid-1980s and the early 1990s, the southward expanding range of the European gypsy moth traversed SHEN and affected all of the University of Virginia's Surface Water Acidification Study (SWAS) study watersheds (Webb 1999). Some areas of the park were heavily defoliated two to three years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. The gypsy moth population in White Oak Run then collapsed due to pathogen outbreak and there was no further heavy defoliation in subsequent years. This insect infestation of forest ecosystems in SHEN resulted in substantial impacts on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over six years before returning to predefoliation levels. Eshleman et al. (2001) estimated that park-wide export of NO_3^- in 1992, the year of peak defoliation, increased 1700% from a predefoliation baseline of about 0.1 kg/ha/yr. The very low levels of NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (e.g., Aber et al. 1989, Stoddard 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (e.g., Likens et al. 1970, Swank 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in SHEN forests.

Although N is thought to play an important role in the chronic acidification of surface waters in some areas (c.f., Sullivan et al. 1997), the elevated concentrations of NO_3^- in SHEN streams following defoliation did not appear to contribute to baseflow acidification in White Oak

Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al. 1995). Both NO_3^- and base cation concentrations increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^-. Episodic acidification following defoliation thus became more frequent and more extreme in terms of observed minimum ANC (Webb et al. 1995).

The full effect of the gypsy moth on aquatic resources in SHEN is not well understood. One consequence may be a reduction in the supply of available soil base cations and associated effects on streamwater ANC. Repeated periods of defoliation would probably increase the impact of episodic acidification on sensitive aquatic fauna and may determine the conditions under which some species are lost. Ultimately such effects may depend upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic outbreaks and collapse (Cambell 1981). It remains to be seen what the long-term pattern will be (Sullivan et al. 2003).

Other pest species can have similar effects. For example, spruce-fir forests throughout the SA have been subjected to significant disturbance, especially from the balsam wooly adelgid (*Adelges piceae*), a European pest which has infested Fraser fir since about the 1960s. Severe fir mortality has occurred in many areas. This disturbance factor has the potential to interact with acidic deposition and other ecosystem stresses, and contribute to multiple-stress tree mortality and to changes in biogeochemical cycling.

3.5.6. Land Disturbance

Watershed disturbances, including road building, agriculture, mining, urbanization, logging, blowdown, and fire can alter various aspects of ecosystems biogeochemistry. Such disturbances can influence the water budget, base cation mobilization, routing of drainage water, nutrient input, and/or S and N cycling in ways that impact the acid-base chemistry and nutrient dynamics of soils and drainage waters (Sullivan et al. 1996). The effects of such disturbances can greatly modify the response of a given watershed to atmospheric inputs of S and/or N.

Examples are numerous. Fire can increase concentrations of NO_3^- and SO_4^{2-} in soils and drainage water (e.g., Riggan et al. 1994, Chorover et al. 1994). Fenn and Poth (1998) hypothesized that successful fire suppression efforts may have contributed to the development of N-saturation in fire-adapted ecosystems in southern California by allowing N to accumulate in

soil and in the forest floor, and by maintaining dense overmature stands with reduced N demand. Blowdown can alter the pathways of drainage water such that a higher proportion of runoff water follows former root channels, thereby reducing the extent of acid neutralization. Disturbances that contribute to erosional losses of soil and/or biomass removal can exacerbate nutrient deficiency problems in the soil. A variety of disturbances can alter N cycling, and cause a delayed response to N enrichment. Where land disturbance has been substantial, it may be difficult or impossible to discern the effects of atmospheric deposition.

3.5.7. Organic Acidity

Organic acids sometimes affect surface water acid-base chemistry, mainly in dilute waters having moderate to high DOC concentrations. Some lakes and streams are naturally acidic as a consequence of organic acids in solution. The presence of organic acids also provides buffering to minimize pH change in response to changes in the amount of SO_4^{2-} or NO_3^- contributed by atmospheric deposition.

Organic acids in fresh water originate from the degradation of biomass in the upland catchment, wetlands, near-stream riparian zones, water column, and stream and lake sediments (Hemond 1994). The watersheds of surface waters that have high concentrations of organic matter (DOC > about 400 µM) often contain wetlands and/or extensive organic-rich riparian areas (Hemond 1990, Sullivan 2000). Organic acids in surface waters include a mixture of functional groups having both strong and weak acid character.

Rosenqvist (1978) and Krug et al. (1985) hypothesized that a significant component of the SO_4^{2-} and NO_3^- contributed from atmospheric deposition merely replace organic anions that were previously present in solution. Under this anion substitution hypothesis, the net result of acidic deposition is not so much an increase in cations (including potentially-toxic H^+ and Al^{n+}) as much as an exchange of SO_4^{2-} and NO_3^- anions for organic anions, with little or no change in ANC and pH.

Hypothesized mechanisms included:

1. decreased mobilization of organic materials from soils and wetlands because of increased H^+ concentration;
2. reduced microbial decomposition of organic materials in soils;
3. changes in dissociation and/or physical structure of humics; and

4. increased loss from solution to sediments through chelation with metals (e.g., Al, Fe) mobilized by increased H^+, and subsequent precipitation of the metal-organic complex (Marmorek et al. 1988, Sullivan 2000).

Recent monitoring data have shown that DOC and organic acid anion concentrations in many lakes have increased in association with decreased S deposition. This response appears to be partly responsible for the limited lakewater ANC and pH recovery that has occurred at many locations.

3.5.8. Cost and Logistics

In an ideal world, study objectives and statistical power would drive monitoring programs. Realistically, it usually comes down to a matter of resources and time. There are usually not enough resources to monitor everything of interest. Generally, there are X dollars available, and at a cost of Y dollars to sample a site one can plan on making X/Y site visits. Choice of sampling a few sites many times or many sites a few times depends on study objectives. Rarely can a monitoring program afford to monitor many sites frequently over time. Questions about spatial extent tend to require sampling many sites, whereas those related to temporal trends require more temporally-intensive sampling, especially if there is a goal to reach conclusions about trends as quickly as possible. The cost to sample a site depends on logistics (transport time to site) and the indicators to be measured (lab costs, and field time [person-hours] on site). The further a site is from the lab and the further it is away from a road, the higher the travel costs. Some indicators of water quality are fairly simple to measure in the field but expensive to measure in the lab (i.e., collection and analysis of water sample) whereas others take a lot of person-hours in the field but have low lab costs (i.e., documentation of fish assemblages). Juggling these varying factors to address multiple, sometimes competing, monitoring objectives is often difficult.

An important logistical consideration is the suitability of protocols for periodic surveys or irregular monitoring. Budgeting and programmatic constraints often preclude regular monitoring, especially monitoring over a long period of time. More often, field data are collected within a schedule that is dictated mainly by availability of funds and staff, and/or the suitability of weather conditions for field activities.

Selection of where to monitor can be an important logistics issue. Often, the more sensitive receptors are located in remote areas that are difficult, expensive, and sometimes

dangerous to access. Ideally, AQRV monitoring sites should be co-located with deposition monitoring equipment. Reality dictates that this is seldom possible.

3.5.9. Variability

Variability in measuring environmental attributes can be ascribed to three causes (Potyondy et al. 2006):

1. measurement errors,
2. environmental heterogeneity, and
3. sampling variance.

Each source of variability can have important implications in the assessment of atmospheric deposition sensitivity or effects. Quantification of each can be included within a sampling quality assurance (QA) plan.

An important aspect of environmental heterogeneity is temporal variability. The acid-base chemistry and certain aspects of the biology (i.e., phytoplankton, zooplankton) of surface waters typically exhibit substantial intra- and interannual variability. Seasonal variability in the concentration of key chemical parameters and in the relative abundance of various life forms often vary by more than the amount of change that might occur in response to acidic deposition. Such variability makes quantification of acidification and recovery responses difficult, and also complicates attempts to evaluate sensitivity to acidification based solely on "index" chemistry or associated biology. The index term is applied to chemical characterization data that correspond with periods when the chemistry is expected to be relatively stable. These are typically summer or fall for lakes and spring baseflow for streams. Although the biological parameters may be more stable during periods when the chemistry is relatively stable, some aspects of biology that are highly sensitive to acidification effects (especially phytoplankton and zooplankton) can be expected to exhibit considerable variability at any time. Variability can be minimized by standardizing the time of sample collection each year, but variability should still be expected. This is an important reason why many years of data are typically required to document biological response.

Lakes and streams also show short-term episodic decreases in ANC, and often also pH, usually in response to hydrological events, such as snowmelt or rainfall. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC to negative values

and increases in inorganic Al in solution to toxic levels. Biological effects can be especially pronounced during episodes.

Rainfall and snowmelt typically pass through the soil profile prior to reaching a stream channel. The typical soil profile in acid-sensitive watersheds has lowest pH in upper organic soil horizons, increasing down the profile to higher pH at depth. Drainage water chemistry is generally at least somewhat reflective of conditions in the lower soil horizons. During high discharge snowmelt or rainfall events, however, flow-routing favors water flowpaths through upper horizons. During such events, drainage water chemistry therefore typically reflects the lower pH, higher organic content, and lower ANC of these upper soil horizons (Sullivan 2000).

The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt water and stormflow water through the watershed. This is what determines the extent of acid neutralization provided by the soils and bedrock in that watershed. High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils are most sensitive to episodic acidification.

Episodes are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO_4^{2-}, NO_3^-, Al^{n+}, organic acid anions, and DOC (Sullivan 2000). These changes in chemistry can adversely impact biota, particularly when changes involve pH, Al_i, and/or Ca^{2+} (Baker et al. 1990c). Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in Al_i in waters having low Ca^{2+} concentration. However, Baker et al. (1990c) concluded that episodes are most likely to impact biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0.

Episodic acidification is nearly ubiquitous in drainage waters throughout the United States (Wigington et al. 1990). Chemical changes during episodes are controlled by both acidic deposition and a number of natural processes, including dilution of base cation concentrations, nitrification, flushing of organic acids from terrestrial to aquatic systems, and the neutral salt effect.

The U.S. EPA's ERP confirmed the chemical and biological effects of episodic pH depressions in lakes and streams in parts of this country (Wigington et al. 1993). The ERP illustrated that episodic processes are mostly natural, that SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition play important roles in the episodic acidification of some surface waters, and that the chemical response that has the greatest impact on biota is increased Al

concentration. Similar findings had been reported elsewhere, especially in Europe, but the ERP helped to clarify the extent, causes, and magnitude of episodic acidification in portions of the United States (Sullivan 2000).

Synoptic lake surveys are typically conducted during the autumn "index period," during which time lakewater chemistry exhibits low temporal variability. Although autumn is an ideal time for surveying lakewater chemistry in terms of minimizing variability, lakewater samples collected during autumn provide little relevant data on episodic processes, and in particular on the dynamics or importance of N as an agent of acidification. Nitrate concentrations in lakewater are elevated during the autumn season only in lakes having watersheds that exhibit fairly advanced symptoms of N saturation (Stoddard 1994).

Research on episodic processes has been conducted mainly on stream systems, which tend to be more susceptible to such effects than lakes. Spatial variability can be considerable in lakes, and this complicates efforts to quantify the magnitude of episodic effects (Gubala et al. 1991). For that reason, few data on episodic chemistry are available for lakes in the areas of concern.

3.6. Recommended AQRVs and Sensitive Receptors

AQRVs are resource elements that could be damaged by air pollution or atmospheric deposition. They include water, flora, soil, cultural resources, geological features, and visibility. For this report, we focus only on measurements of sensitive receptors for the first three of those types of AQRVs. There are many possible sensitive indicators for each AQRV. For example, to protect the AQRV lakewater, sensitive receptors might include the chemistry of the water, which could influence its suitability to support various aquatic species and life forms. There are also sensitive biological indicators, which reflect the suitability of the lakewater for supporting aquatic organisms which might be sensitive to acidification or eutrophication. These could include, for example, fish, zooplankton, or diatoms. A sensitive receptor can be evaluated by taking measurements of indicators of injury or ecosystem change. For example, ANC is an indicator of change in the sensitive indicator water chemistry. An ANC measurement can be interpreted as indicative of damage to water chemistry depending on the biological resource to be protected. For example, in order to protect brook trout in Virginia from probable episodic acidification to ANC values likely to cause harm to the fishery, chronic ANC should be maintained above approximately 20 μeq/L (Bulger et al. 2000). In order to protect species other

than brook trout, a different ANC criterion value (perhaps 50 μeq/L, for example) might be selected as being indicative of probable biological harm.

A limited list of key variables does not exist with which to measure ecosystem condition, or ecosystem response to stressors, such as those associated with atmospheric deposition (i.e., acidification, eutrophication, toxicity). Ecosystems are highly complex, and simply cannot be represented by a handful of variables. Nevertheless, there are variables that have been shown to be, or that are expected to be (based on existing research), reflective of the general level of ecosystem harm that might be associated with atmospheric deposition. We propose a set of consistent AQRVs and associated sensitive receptors that could be used by the Forest Service nationwide for evaluation of ecosystem sensitivity to, and effects from, atmospheric deposition (Table 2). This is by no means an exhaustive list. Individual forests may wish to augment, or replace, some of the listed items in favor of other AQRV receptors that are especially important to a particular forest region or location, or for which that forest has specialized expertise. Nevertheless, the recommended AQRVs and sensitive receptors summarized here are broadly applicable and reflect a range of aquatic and terrestrial effects of atmospheric deposition.

3.7. Development of Protocols

There would be value in development or adoption of national protocols for the Forest Service Air Program to use in monitoring and assessment of the AQRVs, and associated sensitive receptors and indicators, listed in Table 2. This will require decisions regarding what, where, when, and how to measure indicators of the key sensitive receptors, and also associated ecosystem attributes needed to interpret or assess ecosystem status or change in ecosystem status over time.

3.7.1. Key Ecosystem Attributes

There are a relatively small number of ecosystem attributes, or variables, that are routinely selected as candidates to be monitored in order to assess deposition impacts on AQRVs. Ecosystem attributes are characteristics that describe the status of ecosystem features. They can also be used to document changes over time in resource condition. These attributes can be physical, chemical, or biological in nature. Protocols are designated methods for collecting and analyzing data on ecosystem attributes (Potyondy et al. 2006). The combination of attributes and protocols will determine what measurements will be made, how they will be

Table 2.	Straw-person recommended AQRVs, sensitive receptors, and indicators affected by atmospheric deposition of air pollutants for application to Forest Service lands nationwide.		
AQRV	**Sensitive Receptor**	**Indicator/Metric**	**Potential Criteria***
Flora	red spruce (East)	growth decline	change in diameter change in extent of damage
	sugar maple (East)	growth decline	change in diameter change in extent of damage
	lichens	community composition	loss of sensitive taxa
Soil	soil chemistry	base saturation exchangeable Ca^{2+} exchangeable $Ca^{2+} + Mg^{2+}$ C:N molar ratio	BS < 10% % change over time % change over time C:N < 0.2
	soil solution chemistry	Ca:Al molar ratio $[Ca^{2+} + Mg^{2+} + K^{+}]$:Al molar ratio NO_3^- concentration	Ca:Al < 1.0 BC:Al < 1.0 $NO_3^- > 20$ μeq/L during growing season
Surface water	water chemistry	acid neutralizing capacity NO_3^- concentration SO_4^{2-} concentration	ANC < 50 μeq/L $NO_3 > 10$ μeq/L change over time
	water productivity	chlorophyll *a* clarity (lakes)	change over time change over time
	fish	salmonid species presence fish species richness fish condition factor fish Hg concentration fish pesticides(s) concentration	loss over time change over time change over time Hg > 0.3 ppm above threshold values
	zooplankton (lakes)	total zooplankton richness crustacean taxonomic richness rotifer taxonomic richness	change over time change over time change over time
	benthic macroinvertebrates (streams)	mayfly taxonomic richness Index of Biotic Integrity	loss of sensitive taxa Deviation from reference
	diatoms	community composition	historical change from paleolimnological reconstruction

* Metrics can be represented in multiple ways, often as change over time detected in a monitoring program or as exceedence above or below a threshold value. Typically, multiple threshold values are possible. For example, surface water target ANC thresholds are commonly set at 0, 20, or 50 μeq/L to achieve different levels of protection.

made, and how the resulting data will be interpreted when the Forest Service investigates ecosystem impacts from acidic deposition.

3.7.1.1. Aquatic Ecosystems

To achieve the objectives of water quality assessment, we recommend (at a minimum) measurement of the following variables in all lake or stream acid-base water chemistry studies:

<u>Chemical Variables</u>

pH

Gran ANC

Ca^{2+}

Mg^{2+}

K^{+}

Na^{+}

NH_4^{+}

SO_4^{2-}

NO_3^{-}

Cl^{-}

Chlorophyll *a*

Water clarity

Al_i (inorganic monomeric Al; can be omitted if pH is above 6.0)

Specific conductance (optional, but useful for quality assurance evaluation)

DIC (optional, but can aid in ion balance for quality assurance evaluation)

DOC (optional for clear-water systems; important for colored water systems)

Si (optional, but can yield useful information regarding hydrogeology and fish [especially brook trout] spawning suitability)

Total Nitrogen and Total Phosphorus (for evaluation of nutrient criteria/limitation and N enrichment issues)

<u>Biological Variables</u>

Fish species presence and abundance

Zooplankton taxa presence and abundance (lakes)

Benthic macroinvertebrate taxa presence and abundance (streams)

Diatom taxa presence and abundance

3.7.1.2. Terrestrial Ecosystems

Soil

Exchangeable base cations (Ca, Mg, K, Na)

Exchangeable Al

Effective cation exchange capacity (ECEC)

Acidity

% TN

% TC

pH (in H_2O)

Soil Solution

pH

Ca^{2+}

Mg^{2+}

K^+

Na^+

NH_4^+

SO_4^{2-}

NO_3^-

Cl^-

Al_i (inorganic monomeric Al)

Forest Vegetation

Diameter at breast height (periodic measurements)

Growth increment core

Tree damage evaluation

Macro-lichen species present

3.7.2. Example Available Protocols

Detailed protocols should be an important part of any resource characterization and/or monitoring program intended to evaluate atmospheric deposition impacts on AQRVs. Protocols will help to ensure that measured differences among locations or changes over time at one

location actually occur in nature, and are not simply a reflection of different methods, sampling personnel, or timing of sample collection (Geoghegan et al. 1990, Shampine 1993, Geoghegan 1996, Beard et al. 1999, Oakley et al. 2003). Protocols are necessary to ensure data quality and credibility, and to allow determination of temporal trends or spatial patterns in resource sensitivity or level of effect.

3.7.2.1. Survey Design

It may be important to consider protocols for sample site selection. The approach used for sample site selection should be based on study objectives. For objectives related to regional extent of resource conditions and trends in the overall resource over time, it can be important to use a statistical design. For example, the U.S. EPA Environmental Monitoring and Assessment Program (EMAP) program has developed survey design protocols for aquatic resources that may be used to select sites so that estimates can be made from survey data for the entire resource of interest. In this design, sample sites are selected randomly from a frame (GIS coverage of resource of interest) with a systematic spatial component using a GRTS (generalized, randomized, tessellated, stratified) design (see Stevens and Olsen 2004, Olsen et al. 1999, Herlihy et al. 2000). The strength of this design is that it allows robust estimates of regional condition for any measured stressor or response. For example, you may be able to conclude that X% of the stream length (or Y% of the lakes) in the ABC National Forest have pH < 6. Employing this type of survey design does require some up-front office costs for fixing the resource frame (a GIS layer depicting the resource of interest) and running the statistical design algorithms. It also requires going to randomly selected sites which in some instances may have difficult site access. This type of regional design should be considered whenever the population of interest is too large to census and regional results are of importance. Paulsen et al. (1998) reported on a number of case studies illustrating that extrapolating regional condition from non-random survey data can lead to erroneous conclusions.

3.7.2.2. Field Protocols

Field protocols can be broken down into chemical, biological, and physical habitat methods. Physical habitat protocols are perhaps the most complex but they are not relevant to AQRV and deposition impacts so they will not be discussed here. Chemical protocols will be discussed in relation to sampling soil, water, and fish tissue for chemical analytes. Biological

protocols will be discussed in relation to species and community assemblage presence for fish, amphibians, macroinvertebrates, zooplankton, periphyton (algae/diatoms), lichens, and forest trees.

3.7.2.2.1. Tested National-Scale Survey Protocols

At the national scale, both EMAP and the U.S. Geological Survey's (USGS) National Water Quality Assessment Program (NAWQA) have been collecting water quality data nationwide since the early 1990s. Both EMAP and NAWQA have published field protocols for aquatic sampling that have been field-tested for a number of years under fairly rigorous QA plans. Due to their national scale, they have been applied to a wide variety of types and sizes of aquatic systems. NAWQA focus is on lotic systems, whereas EMAP has sampled streams, rivers, lakes and estuaries. Recently, EPA's Office of Water conducted a national study of over 1,000 randomly selected wadeable stream sites, using EMAP protocols (U.S. EPA 2006).

EMAP and its smaller scale regional counterpart (Regional EMAP or REMAP) have been conducting probability-based surveys to determine the ecological condition of streams and rivers in many parts of the United States for about 15 years. In EMAP, sample sites are selected using a systematic, randomized sample providing a sound statistical basis for assuming that the data are representative of all the streams and rivers of the study region (Hughes et al. 2000). Thus, condition estimates can be extrapolated to the entire resource (e.g., stream network, lake population). Sites were sampled for a suite of biological, chemical and habitat indicators of ecological condition. EMAP has published protocols for streams (Peck et al. 2006), rivers (Peck et al. 2003), and lakes (Baker et al. 1997).

NAWQA is designed to assess the condition of the nation's streams and groundwater and how natural and human factors affect condition (Gilliom et al. 1995). NAWQA sampling has taken place within 50 major hydrologic basins across the country. Within each basin, sites were hand-picked, with smaller streams being indicator sites selected to represent relatively homogenous environmental settings and larger streams/rivers used as integrator sites affected by complex combinations of land-use and natural influences. A series of USGS reports document the biological field methods (Moulton et al. 2002), water sampling field methods (Shelton 1994), and laboratory methods for macroinvertebrates (Moulton et al. 2000) and periphyton (Charles et al. 2002).

In addition to the protocols developed for these national surface water surveys, the EPA Office of Water has developed and published Rapid Bioassessment Protocols (RBP) for fish, macroinvertebrate and periphyton sampling (Barbour et al. 1999). The RBP were initially developed in the late 1980s to provide basic aquatic life data for water quality management purposes such as problem screening, site ranking, and trend monitoring. The RBP were not meant to provide the rigor of fully comprehensive studies, but were designed to supply pertinent, cost-effective information when applied in the appropriate context. These protocols proved useful to EPA and the States in developing biocriteria programs and were revised in 1999 to reflect advancements in bioassessment methods. The current manual (Barbour et al. 1999) provides an updated compilation of the most cost-effective and scientifically valid approaches. In addition, many state agencies have established synoptic aquatic biomonitoring programs with their own field protocols. We will mention some of the state protocols but a comprehensive review of all state protocols is beyond the scope of this report.

3.7.2.2.2. Biological Protocols

3.7.2.2.2.1. Sample Reach Length

Unlike water chemical measurements which can easily be collected at a single sampling point, it is impossible to sample most aquatic biology at a single point on a stream or lake. Thus, biological sampling requires setting up some kind of sampling reach (or plot scale design) to adequately characterize the site biota. In EMAP, stream sampling is done along a reach that is 40 times the mean wetted width (a minimum of 150 m in small streams). Sample reach lengths in NAWQA were 150-300 m for wadeable streams and 500-1000 m for larger, nonwadeable streams (Meador et al. 1993). States typically use similar sample reach lengths; Ohio EPA requires 150-200 m in streams and 500 m in rivers. Sample reach lengths in Iowa streams were 150-320 m, depending on width and habitat form. Stream reach lengths for EMAP were set from effort-return studies that showed that sampling of reach lengths 40 times the mean wetted width captured over 90% of the species in western Oregon streams (Reynolds et al. 2003). Rivers in EMAP were sampled along longer reaches (100 times the mean wetted width) to achieve a similar sampling sufficiency (Hughes et al. 2002).

3.7.2.2.2.2. Fish Assemblages

For streams and rivers, the EMAP and NAWQA fish protocols were designed to characterize the entire fish assemblage at each sample site. Fish sampling methods varied somewhat among surveys but all involved sampling a defined sample reach length and identifying and enumerating all captured individuals. Electrofishing is the normal method of fish sampling, although data may be collected by seining in cases where the conductivity is too high or low, there are permit issues, or other reasons favoring non-electrical methods. The goal is to capture a representative sample of the fish assemblage in the study reach. Streams are typically sampled with backpack electrofishing units whereas rivers are sampled with raft-mounted units. Some protocols specify that the ends of the stream sample reach be block netted to prevent fish from leaving the sample reach during the sampling period.

Streams are sampled by walking upstream, whereas raft sampling of rivers is conducted by floating downstream. In both cases, fish are netted after being stunned and then are placed in an aerated bucket or enclosure until they are processed. Processing occurs at intermittent intervals throughout the reach sampling. In EMAP, processing consists of recording a running tally of the number of individuals of each species caught, the minimum and maximum total length, and the presence of anomalies (DELT-deformities, eroded fins, lesions, tumors). A subset of individuals is preserved and used as voucher specimens for confirmation of species identifications at a fish museum. Also, individuals (or a subset of them) that could not be identified in the field are vouchered for museum identification. For later calculation of catch per unit effort (CPUE), the total fishing time and shocking time for the reach are also recorded along with shocker settings.

Sampling fish in lakes is more complicated and usually requires multiple gear types and more field effort. In the EMAP lake fish sampling protocol, field teams collect fish using overnight sets of trap nets and minnow traps, and gill netting/seining after sunset. Within the lake, sampling is conducted in every major habitat type regardless of its expected productivity. This requires that crews identify and map major habitat types before sampling. Fish sampling is stratified by habitat and is random within habitats. The number of fish sample sites within each habitat is related to lake size. Collected fish are identified to species, and examined for external gross pathology (DELT). Long-lived species are measured for length. Small fish are preserved for species confirmation and museum vouchering. Fish sampling in the EMAP Northeastern Lake study typically took 2-3 days per lake.

All of these fish protocols provide a CPUE estimate of fish abundance at a site but do not give estimates of total population numbers or biomass. Sampling for total population estimates at a site is more time consuming and requires either multiple passes or some kind of mark recapture survey technique.

3.7.2.2.2.3. Amphibians

Amphibians can be sampled in both the aquatic and terrestrial environment. In EMAP and NAWQA, amphibians that are captured in the water as part of the stream/river fish sampling are identified and recorded in a manner similar to fish. The various amphibian species present are often analyzed together as a vertebrate indicator. Neither EMAP nor NAWQA has field protocols for sampling amphibians in the terrestrial environment.

3.7.2.2.2.4. Macroinvertebrates

Macroinvertebrate stream sampling protocols are very simple in essence and consist of compositing a number of different stream samples from the study reach together and then counting and identifying the captured macroinvertebrates. However, there are many methods by which this can be accomplished and a variety of existing field protocols for macroinvertebrate sampling. In particular, the different approaches include the following types of variation:

Sampling device: There are samplers that involve netting and collecting invertebrates on a single occasion (e.g., kick nets, Surber and Hess samplers) and those that involve leaving something in the stream for a set period of time and then collecting it and counting the bugs that colonized the artificial substrate (e.g., rock bags, Hester-Dendy plates).

Stream habitat sampling: Where in the stream do you collect the sample? There are protocols that target one specific habitat type (e.g., riffles, wood, snags, margins, or vegetation), multiple separate samples of some number of different habitat types, judgment samples (richest targeted habitat, habitat-proportional sampling), or one single reach-wide composite.

Mesh size: The diameter of the mesh in the net varies from protocol to protocol. Mesh size helps to differentiate what organisms are micro and pass through the net from those that are macro-invertebrates and stay in the net.

Composite size: The number of different sites sampled in the stream that go into the reach composite sample varies from protocol to protocol. The goal is to sample enough different

places in the study reach to generate a representative sample of the macroinvertebrate population of the targeted habitat.

Field versus laboratory ID: There are some protocols that require counting and identifying samples in the field where picking the individuals is easier (they move around) and they aren't damaged by sample handling and transport. This requires more field time and a trained taxonomist in the field crew. Most protocols specify that the samples be preserved with ethanol and processed in the lab.

Taxonomic resolution: A determination needs to be made as to what taxonomic level the macroinvertebrates will be identified. This can often vary by class of organism. Common levels of resolution are family or genus. Species level of identification for the majority of captured individuals in stream macroinvertebrate samples is often impossible due to specimen damage, the lack of features of some tiny early instars, and the lack of comprehensive species level keys. Some protocols specify lowest practical taxonomic resolution, which is the lowest possible resolution for each specimen with reasonable effort. Of particular concern for bioassessment is whether the Chironomids (midge family) are identified to genus or left as one family. Chironomids typically make up a large part of the sample and this one family has hundreds of different genera.

Fixed count/subsampling: Macroinvertebrate samples can contain very few or tens of thousands of individual organisms. In some protocols, the entire field sample is enumerated and identified. Other protocols spread the sample out on a gridded counting tray and process random grids until some fixed number of organisms are counted (common fixed count numbers are 100, 300, or 500 individuals). Usually, entire grids are counted so that by knowing the proportion of grids counted to total grids on the tray one can make estimates of actual number of individuals in the sample. In addition, some protocols specify that a "large, rare" search be conducted on any portion of the sample not used in the fixed count. If any large and/or rare taxa were found that were not in the fixed count sample they are recorded separately.

<u>EMAP Streams</u>

The EMAP stream protocol for macroinvertebrate sampling is based on compositing 11 kick net samples (using a 500 μm mesh modified D-frame dip net) along the study reach into a single composite sample. The 40 channel width study reach laid out for fish sampling is divided into 11 equal interval transects (each four channel widths apart) and a 1 ft^2 surface area kick net

sample is taken at each transect, working in the upstream direction. At each sampling location, individual kick net samples are taken from the left, center, or right portion of the transect. At the first transect, the left, center or right portion is sampled; the decision is made randomly. Subsequent sampling alternates in progressive left-center-right order in succeeding transects. The samples from all 11 transects are composited into one sample, preserved in ethanol, and transported to the lab for processing. In the laboratory, a 500-individual fixed count protocol is used to enumerate the macroinvertebrates. The target level for identification is genus for most taxa, including Chironomids.

NAWQA

The NAWQA macroinvertebrate protocol specifies collection of two types of samples in the study reach. The first is a semi-quantitative sample, collected to provide a measure of relative abundance of the invertebrate taxa living in the richest targeted habitat (RTH) in the reach (the most species-rich, typically coarse riffle or woody snag habitat). The RTH sample consists of a series of discrete collections that are processed and combined into a single composited sample. The second sample type is a qualitative multihabitat sample (QMH) that is collected to document the invertebrate taxa that are present throughout the sampling reach. A discrete QMH collection is taken from each of the different in-stream habitats that are present in the reach. These discrete collections are then processed and combined into a single composited sample. The NAWQA protocols describe 51 possible habitat types within three levels of organization. RTH composite samples consist of either five, similar type (velocity, substrate, depth) 0.25 m^2 riffle (coarse-grained natural-bed) samples taken with a Slack sampler (500 µm mesh rectangular net), 10 snag samples from five different woody snags, or five grab samples (Ponar or Eckman dredge) from fine-grained natural-bed substrate. Snag samples are taken when riffles are not present and fine-grained samples are taken when neither riffles nor snags are present. QMH samples are taken by allocating sampling effort in proportion to habitat occurrence within the sample reach. QMH sampling effort is based on time, with a 1 hour maximum effort. Samples are preserved with 10% buffered formalin.

EMAP Rivers

The EMAP river protocol is identical to the stream protocol with the exception of where the sample is collected in the field. In each river, the kick net samples are collected at each of the 11 transects from the wadeable margin of the river, near the shoreline.

EMAP Lakes

In EMAP, lake macroinvertebrate sampling is restricted to the sublittoral zones of lakes in weed-free areas where possible. Single soft sediment core samples are taken at 10 equally distant sampling sites located around the perimeter of the lake. The actual site location for benthic sampling is determined from the vertical distribution (depth profile) of temperature and DO. In thermally stratified lakes, samples are taken in well-oxygenated areas (where DO is greater than 5 mg/L and at sites where the upper limits of the metalimnion meet the lake bottom) or within the metalimnion where dissolved oxygen concentration still exceeds 5 mg/L. The dissolved oxygen value of 5 mg/L is operationally defined and is intended to ensure that samples are collected from the sublittoral zone rather than from locations that might be more characteristic of the profundal zone.

EPA Rapid Bioassessment Protocol

The RBP describes multiple recommended protocols for macroinvertebrate sampling. A 100 m sample reach is identified and two habitat sample types are described. The single habitat protocol is taken from riffle/run habitat consisting of composites of multiple kicknet samples from different velocity regions that sum to at least 2 m^2 surface area. The multi-habitat sample was instigated by benthologists in low gradient streams. This sample consists of 20 dip net "jab samples," with the 20 jabs being allocated across habitats (cobbles, vegetation, snag, macrophyte, sand) in the proportion in which they occur throughout the study reach. Composite samples are preserved in ethanol and counted in the lab with a recommended 200 fixed count protocol. It is noted that the fixed count may be of different size if desired. Identifications are to either genus or family depending on the project objectives.

3.7.2.2.2.5. Periphyton (Algae/Diatoms)

Periphyton includes algae, fungi, bacteria, protozoa, and organic matter associated with stream channel substrates. Periphyton are useful indicators of environmental condition because

they respond rapidly to changing conditions and are sensitive to many anthropogenic disturbances, including habitat destruction, contamination by nutrients, metals, herbicides, hydrocarbons, and acidification. Periphyton sampling in streams is done by fewer agencies than macroinvertebrate sampling. It is, however, used by both EMAP and NAWQA as well as a few state agencies (e.g., Montana and Kentucky). Sources of field protocol variations for periphyton are very similar to those listed for macroinvertebrates in the previous section.

In the EMAP stream and river periphyton protocol, 11 equal interval transect periphyton samples are collected from each study reach in the same location as the macroinvertebrate samples. These are combined into one composite sample per site. At each transect, a coarse substrate sample is collected if coarse substrate is available. If not, a fine substrate sample is collected. Coarse substrate is sampled by removing the substrate from the water and placing a 3.8 cm diameter (12 cm^2 area) by ~2 cm high PVC pipe ring on part of that substrate that was receiving light and scraping the area inside the ring with a toothbrush to loosen the attached periphyton. Loosened material is then rinsed into the sample bottle using a funnel and squirt bottle. Fine substrate is sampled by placing the 10 cm diameter ring on top of the substrate and sucking the fine surface layer that is inside the ring into a 50 mL syringe and then placing the syringe contents into the sample bottle. At the end of the field sampling, the composite sample volume is recorded, mixed well and a 50 mL aliquot placed in a 50 mL centrifuge tube. It is then preserved with buffered formalin and sent to the laboratory for species identification and enumeration. Other aliquots are also collected, filtered in the field, and the filter kept on ice and sent to the laboratory for chlorophyll and biomass analysis. Taxonomic identification of diatoms is done using a fixed 500 valve count to species or species variant level. Soft bodied algae are identified separately, usually to genus.

In lakes, numerous researchers have used sediment diatoms as indicators of lakewater condition, particularly as indicators of acid-base and nutrient status. By using stratigraphy and dating of sediment cores, it is also possible to do historical reconstructions of changes in lake condition over time in lakes with sediment that is amenable to collection of a sediment core.

In EMAP lakes, one sediment core is collected to assess both the current (surface sediment) and pre-industrial diatom community (core bottom). The sediment core is collected with a box corer from the deepest part of the lake. If there is not soft sediment present from which to collect a core, field crews search for a station that has soft sediment. In the Northeast, the target core length is 35 to 45 cm. Cores are extruded in the field into two samples. The top 1

cm is placed in one sample bag, and a 1 cm slice 3 cm above the bottom of the core is placed in another bag. Samples are kept on ice or refrigerated during storage and shipping.

In NAWQA flowing waters, habitat type samples for periphyton analysis are defined in the same manner as the NAWQA macroinvertebrate sampling with a qualitative multihabitat sample (QMH) and richest targeted habitat sample (RTH). In addition, a deposition targeted habitat sample (DTH) is also collected when that habitat is present. As in EMAP, coarse substrate is sampled with a fixed area ring and scraping with a brush. In NAWQA, five cobbles from each of five different locations in the reach are scraped and composited into a single reach sample when the RTH is coarse substrate. For woody snag RTH, five pieces of wood are collected from different parts of the reach with pruning shears or a saw. The five wood pieces are processed and composited together by scraping with the ring method when possible or by scrapping the entire piece of wood and recording the piece diameter and length. The DTH fine sediment (sand or silt) sample is collected by compositing sediment from five locations in the reach. Sediment is collected by pressing an inverted Petri dish lid (~ 47 mm diameter) into the sediment and sliding it on top of a spatula. The QMH sample is collected by brushing, scraping or siphoning submerged substrate from five different periphyton habitats; epilithic, epidendric, epiphytic, episammic, and epipelic. The final QMH composite sample is made by combining these five habitat subsamples into one sample in proportion to their abundance in the study reach. As in EMAP, aliquots of the various composite samples are taken for taxonomic identification, chlorophyll, and biomass.

3.7.2.2.2.6. Zooplankton

Zooplankton are collected in EMAP lakes using two nets (202 µm coarse mesh and 48 µm fine mesh) in bongo configuration (side by side). One vertical tow is made with the nets in the deepest part of the lake from 0.5 m above the bottom to the surface of the lake. In lakes less than 2 m deep, two tows are made. Care must be taken to prevent collection of any bottom sediment into the net. The samples from each net are placed in separate bottles and narcotized with alka-seltzer before preservation in the field with a buffered formalin/sucrose solution.

3.7.2.2.3. Water Chemistry Protocols

Water chemistry data can be used to characterize acid-base status, trophic condition, chemical stressors (e.g., excessive conductivity, SO_4^{2-} from mining activity, or chloride derived

from human land use activities), and to classify sites based on their water chemistry and the likelihood that they are impacted by acidification from atmospheric deposition. Field protocols for water chemistry are generally fairly simple. A water sample is collected and sent to the laboratory for analysis. In situ measurements are usually made with various kinds of meters that need to be calibrated and maintained according to manufacturer's instructions. Decisions about bottle type, required sample volumes, filtration/preservation, and holding times are dependent on the specific analyte, laboratory, and project goals. The main field protocol decision is whether to take a single grab water sample or to take some kind of width and/or depth-integrated composite water sample.

In EMAP, water chemistry information includes measurements of the major cations and anions, nutrients, turbidity and color. Syringe samples are collected for laboratory analysis of pH and dissolved inorganic carbon (DIC). Surface water is collected in one 4-L container and two 60 mL syringes that are stored on ice in darkness and shipped or driven to the analytical laboratory within 24 hours of collection. Overnight express mail for these samples is required because the syringe samples need to be analyzed, and the 4-L bulk sample needs to be stabilized (by filtration and/or acidification) within a short period of time (72 hours) after collection.

Syringes are used to protect samples from exposure to the atmosphere because the pH and DIC concentrations can change if the sample water equilibrates with atmospheric CO_2. Lab syringe pH was found to be more precise than field pH in EPA's acid rain surveys (National Surface Water Survey - NSWS).

In EMAP streams, samples and in-situ measurements are obtained at a single sampling location below the surface at mid-channel in an area of flowing water. Spatial variability across the channel of a single stream is expected to be minimal in wadeable streams as compared to the variability expected among sites, so EMAP does not require a composite water chemistry sample. Longitudinal variability at small scales (on the order of 0.5 km), appears to be minimal based on conductivity data taken systematically along several larger stream reaches in the Mid-Atlantic region. In EMAP lakes, samples are collected from 1.5 m depth (0.5 m in lakes < 2 m deep) at a station located in the deepest part of the lake. Two samples are collected into 6 L Van Dorn bottles. The first is used for the water chemistry samples. The second Van Dorn is used to collect water to filter in the field for measurement of chlorophyll-a. Most of the EMAP procedures have been adapted from the NSWS field operations handbook (U.S. EPA 1989).

NAWQA samples are collected using depth and width integrating techniques. Collection sites are located in relatively straight channel reaches where the flow is uniform. Sampling directly in a ripple or from ponded/sluggish water is to be avoided. Sites upstream or downstream of confluences or point sources are also avoided to minimize problems caused by backwater effects or poorly mixed flows. The equal-width-increment (EWI) sampling method is the recommended procedure for NAWQA. The EWI method requires equal spacing of a number of verticals across the cross section and an equal transit rate, both upward and downward, in all verticals. The stream width is divided into a number of equal-width intervals; the number of intervals is dependent on results of water-quality profiles, uniformity of sediment distribution, channel width, and the depth and velocity distribution across the stream. Five to ten increments are used for cross sections less than 5 ft wide and a minimum of 10 increments in streams 5 ft wide or greater. A maximum of 20 increments are used in extremely wide, shallow cross sections. The sample verticals should be spaced at least 6 in apart. Samples from several verticals may be accumulated in the same bottle. However, abbreviated sampling methods (that is, weighted-bottle or dip sample) are sometimes used in NAWQA as the best procedure for collecting a sample representative of the stream chemistry in some conditions.

For AQRVs, mercury contamination in fish tissue is probably the element of most concern. Mercury is ubiquitous. In a recent survey of western fish from EMAP probability survey data, all 2,700 fish in the survey had detectable levels of mercury (Peterson et al. 2007). Mercury levels in fish are strongly related to fish age (size) and vary widely by species depending on their position in the food web. Large, piscivorous fish (e.g., bass, pikeminnow, walleye, pike) have the highest mercury levels because they bioaccumulate the most mercury. Fish species and size need to be taken into account in any regional analysis of fish tissue mercury data. Ideally, if the goal of the sampling is to compare levels of mercury contamination across sites, the same size and species of fish should be sampled everywhere. However, that is often impossible in a large-scale survey.

Field fish tissue contamination protocols are fairly simple. A representative sample of fish is collected, frozen and transported to the lab on ice. The major protocol decision is what fish to collect as “representative” for analysis (species and size). In the EMAP lake and stream surveys, fish for tissue analysis are taken as part of the fish community electrofishing sample. A big fish sample and a small fish sample are collected from each study reach. The big fish sample (total length ≥ 120 mm) consists of three fish of varying lengths from each of three species. The

small fish (total length < 120 mm) sample consists of one composite sample of multiple small fish of the same species as needed to provide 50 g of fish. The field protocol lists target species in order of priority to guide crews in species selection. Such a list is dependent on the specific survey region and objectives.

One important distinction to make in fish tissue sampling is whether to measure contamination in whole fish or fish fillets. Whole fish analysis may be more relevant in evaluating wildlife effects, whereas fish fillets may be more relevant to human consumption. There is a strong relationship between fillet and whole body mercury concentrations so that it is possible to measure one and infer the other (Peterson et al. 2007). There are also new biopsy techniques available that involve taking a small biopsy sample from the fish in the field for analysis. Studies have shown good agreement between biopsy and whole fish mercury concentrations (e.g., Peterson et al. 2005). The major advantages to the biopsy sample are that it is non-lethal to the fish and it greatly reduces the shipping and storage issues involved with large numbers of frozen fish.

3.7.2.3. Forest Health Monitoring Program Protocols

Protocols for vegetative plot assessment within the Forest Health Monitoring Program are available on the FIA website (www.fia.fs.fed.us). Information is provided regarding plot establishment and location; collection of tree, sapling and seedling data; and tree damage assessment.

3.7.2.4. Examples of Existing Regional or Local Protocol Documents

There are countless protocol documents and monitoring procedure summaries associated with various national forests, national parks, and state agencies. They vary in scope, level of detail, and specificity. We do not attempt to summarize the guidelines for all of these programs. Rather, we attempt in this section to highlight some of the regional and local protocols that are available from various federal agencies and a few of the more noteworthy programs that are associated with more geographically-limited areas. Below we highlight a number of existing regional and local (forest- or park-specific) protocol documents, especially those associated with relatively large regional monitoring programs conducted by federal agencies. Many of these may prove to be helpful in the design and adoption of national protocols for the Air Program.

Guidelines for development of federal monitoring protocols

Oakley et al. (2003) developed guidelines for the content and format of monitoring protocols. These guidelines have been adopted by the NPS Inventory and Monitoring Program and the USGS Status and Trends Program for monitoring within national parks. In the words of Oakley et al. (2003), "Designing a monitoring project is like getting a tattoo: you want to get it right the first time because making major changes later can be messy and painful." Properly designed and documented protocols for the Forest Service Air Program will improve the comparability of data at different times and from different locations. This will be critical to the process of integrating environmental monitoring efforts within and between government agencies (Committee on Environment and Natural Resources 1997).

Water chemistry protocols for high-elevation western lakes

Turk (2001) authored a field guide for surface water sampling for the Forest Service Air Program. It discussed the supplies, instruments, and methods of collection to be considered for surface water sampling programs. The major focus was on wilderness sampling in the mountainous western United States. This field guide was intended to supplement material summarized by Fox et al. (1987), which had described a common set of protocols to facilitate inventory and monitoring in wilderness within the Air Program. Turk (2001) described sample collection procedures; field measurements of dissolved oxygen, water temperature, pH, specific conductance, and secchi disk depth; sample handling; and quality assurance.

Protocols for collection of data to support MAGIC model applications

Webb et al. (2004) developed protocols for the collection of streamwater chemistry and soil acid-base chemistry data for the Cherokee, Pisgah, Nantahala, and Sumpter National Forests. The purpose of these protocols was to guide the collection of data that would be useful in meeting the data input requirements of the MAGIC model. MAGIC applications in this region are often intended to identify which watersheds might experience soil base cation depletion, to identify which watersheds experience streamwater chemistry that is inhospitable to fish, and/or to estimate critical loads of acidic deposition that will protect or restore the biological integrity of acid-sensitive watersheds. Webb et al. (2004) summarized equipment and materials needed by sampling crews, site location and documentation, sampling logistics, sample handling, laboratory analysis, and sampling safety issues.

Protocols for western wilderness lake watersheds

Fox et al. (1987) provided guidelines to the Forest Service for measuring the physical, chemical, and biological conditions of wilderness lakes and watersheds in the western United States. The Fox et al. (1987) report represents the consensus product of a workshop attended mainly by federal agency scientists having air resources management responsibilities. The guidelines were developed in response to the perceived need for standardized measures to determine if significant changes are occurring in wilderness areas in order to comply with regulations such as the Clean Air Act and the Wilderness Act. Credible protocols are necessary to provide the basis for making sound decisions in the regulatory, legal, and management arenas.

Information is provided in the report regarding regulatory and management constraints in wilderness areas. Protocols are provided for application to high-elevation Class I wilderness areas throughout the western United States for the protection of air quality related values (AQRVs). Guidelines are intended to provide the basis for determining the existing status of AQRVs, monitoring for changes over time, and evaluating whether changes are naturally-occurring or the result of human-caused air pollution and atmospheric deposition.

Specific protocols are summarized for measuring key aspects of six effects areas:

- atmospheric environment
- visibility
- soils and geology
- aquatic chemistry
- aquatic biology
- plants

In particular, protocols are outlined that are protective of wilderness values. Thus, measurements are easily obtainable within the wilderness by primitive means. Important constraints include weather, season, animal damage to equipment, remote locations, and lack of power.

Guidelines for monitoring AQRVs in lakes and streams in national forests

Eilers (2007) provided guidance for standardizing monitoring procedures for evaluation of surface water AQRVs in national forests. The focus of this report is mainly on monitoring objectives, potential confounding factors, monitoring intensity, and sampling frequency. The

report describes existing field and laboratory protocols for routine monitoring, plus additional metrics that might be considered for more intensive study.

USGS Water Quality Field Manual

The USGS Office of Water Quality produced a National Field Manual for the Collection of Water Quality Data (USGS, variously dated). It provides guidelines and standard procedures for USGS studies designed to assess the quality of surface water and ground water resources throughout the United States. Each chapter is published separately and revised periodically (http://pubs.water.usgs.gov/twri9A). Formal training and field apprenticeship are required in order to correctly implement the USGS protocols and guidelines. Individual chapters address the following topics:

1. Preparation for water sampling
2. Selection of equipment
3. Cleaning of equipment
4. Collection of water samples
5. Processing of water samples
6. Field measurements
7. Biological indicators
8. Bottom-material samples
9. Safety in field activities

Shenandoah Watershed Study Field Manual

The Shenandoah Watershed Study (SWAS) has been monitoring streamwater chemistry in several streams in Shenandoah National Park for over two decades to document the effects of acidic deposition. The SWAS Field Manual outlines field and laboratory procedures. These include measurement of pH, Gran ANC, monomeric Al, DOC, and major ions. The SWAS chemical methods were also used in the Virginia Trout Stream Sensitivity Study (VTSSS).

Screening criteria to identify wilderness areas having acid-sensitive lakes

Rutkowski et al. (2001) described coarse-scale GIS analyses to determine the vulnerability of wilderness areas to having low-ANC lakes on a regional scale. The objective was to provide a cost-effective screening tool to help focus field sampling activities intended to characterize, and then monitor, acid-sensitive wilderness lakes. The analysis considered the

number of lakes present and general sensitivity of the regional bedrock. Fine-scale analyses were then used to identify the location of probable low-ANC lakes. Bedrock geology, vegetative cover, and elevation were found to be significant predictors of low-ANC lakes.

Screening procedure for identifying acid-sensitive lakes

Berg et al. (2005) described methods for analyzing watershed characteristics in order to identify lakes in the Sierra Nevada that would have a high probability of being acid-sensitive. Watershed-to-lake area ratio, lithology, vegetation cover, and headwater location were all significant variables in identifying lakes that had low ANC. This approach provides a cost-effective way of locating low-ANC candidate lakes for research or monitoring.

Air pollution-related lichen monitoring guidelines

Blett et al. (2003) summarized guidelines for lichen monitoring in order to support federal agency regulatory and management efforts. Procedures are generally described for using lichens as indicators of ecosystem health, based on occurrence or abundance of sensitive species. Approaches are also described for using lichens as passive monitors of ambient levels of air pollution, based on tissue analyses of species that are relatively insensitive to air pollution. Lichen studies on federal lands throughout the United States are summarized.

Protocols of the Forest Service Air Program's Water, Ozone, and Soils Laboratory

The Air Program of the Forest Service maintains a high-quality Biogeochemistry Analytical Laboratory in Fort Collins, Colorado. This lab analyzes samples of surface water, precipitation, soil water, and snow. In particular, the lab is set up to handle very dilute water samples, with detection limits for major ions ranging from 0.01 mg/L (Na^+, NH_4^+, F^-, Cl^-) to 0.05 mg/L (SO_4^{2-}). The detection limit is defined as three times the standard deviation of 10 non-consecutive reagent or calibration blank analyses[3]. Further description of laboratory methodologies is provided on the laboratory website (http://www.fs.fed.us/waterlab/). Recommended field sampling protocols are also included. General sample collection methods are described, including procedures for avoiding contamination of lake or stream samples.

[3] If a signal is not produced, a low-concentration standard can be analyzed to quantify detection limit.

Protocols for storage and filtration of water samples

Korfmacher and Musselman (2006) evaluated protocols for storage and filtration of surface water samples collected from remote alpine and subalpine locations in the western United States. Sampling in such areas presents special challenges because of complex sample collection logistics. Various previous federal agency protocols have called for field filtration for some analytes (US EPA 1996, Turk 2001). Others have found on-site sample filtration to be impractical (Messer et al. 1986) or to unnecessarily increase the risk of sample contamination (Fox et al. 1987). Other disadvantages of on-site filtration include increased cost and complexity of sampling procedures and greater training requirements for field staff.

Korfmacher and Musselman (2006) did not find any analytes to show significant changes in concentration when stored less than 48 hrs. When storage time exceeded 48 hrs, pH, Na^+, NH_4^+, K^+, Cl^-, and SO_4^{2-} exhibited small, but statistically significant, changes in concentration. Ca^{2+} and NO_3^- concentrations were significantly higher in field-filtered samples, as compared with laboratory filtration, but the differences were small. They concluded that the small differences did not justify the added expense, training, and risk of sample contamination associated with field filtration.

National Park Service Vital Signs Monitoring Networks

The NPS has been involved in selecting and prioritizing candidate “vital signs” for various types of ecosystems. Designated vital signs comprise a subset of physical, chemical, and biological elements of national park ecosystems that are selected to be representative of ecosystem health, sensitive to human-caused stressors, and/or that are important to park visitors. For example, important biological vital signs might include aquatic biota or vegetation community composition; aquatic system vital signs might include water chemistry or snowpack (http://science.nature.nps.gov/im/monitor/). As part of this vital signs effort, various monitoring protocols are under evaluation and development (c.f. Oakley et al. 2003).

The NPS monitoring protocols database (http://science.nature.nps.gov/im/monitor/protocoldb.cfm) will eventually contain all protocols used by the NPS Vital Signs Monitoring Networks (Ellen Porter, NPS, pers. comm., December 2006). As part of that effort, the NPS Air Resources Division in Denver is currently working on development of a snow sampling protocol,

a throughfall protocol, and various protocols for toxics (contacts: Ellen Porter and Tamara Blett, NPS, Denver).

Multiagency approach to evaluation of acidic deposition thresholds

Deposition analysis thresholds have been developed by federal land managers (FLMs) for evaluating the general level of possible impact from new S sources (c.f., FLAG 2002). Such thresholds are recommended for screening purposes, as the first step in analyzing whether measures should be taken to ensure protection of sensitive environmental resources. This is done as part of the New Source Review permitting process. It is intended to be used in the context of evaluating numerous existing and potential future S sources, and therefore these initial screening criteria are typically based on low values for atmospheric deposition. The screening value for S deposition is *not* proposed as a threshold for harm, but rather to determine if a Prevention of Significant Deterioration (PSD) applicant should use models for subsequent analysis in conjunction with the PSD application process (USFS 2000). Similarly, a deposition analysis threshold (DAT) based on an estimate of background pre-industrial deposition, is a deposition threshold, not necessarily an adverse impact threshold (FLAG 2002). It is recommended as a level of additional deposition that triggers management concern about a PSD application, not necessarily the amount that constitutes an adverse impact to the environment" (FLAG 2002).

Agency scientists are currently working on revisions to the FLAG 2000 report, including some that will affect deposition sensitivity components. The expected changes include added discussion of Deposition Analysis Thresholds (DATs) and Concern Thresholds for S and N deposition, and also an expanded discussion of critical loads to reflect significant developments since publication of the FLAG 2000 report (John Bunyak, National Park Service, pers. comm., December, 2006).

The Federal Land Managers' Air Quality Related Values Workgroup (FLAG) was formed by the USDA Forest Service, National Park Service, and U.S. Fish and Wildlife Service, the three agencies that administer Class I areas. The objective is to develop a more consistent approach for Federal Land Managers (FLMs) to evaluate air pollution effects, particularly in regard to the New Source Review Program and the review by FLMs of Prevention of Significant Deterioration (PSD) of air quality permit applications. The FLAG Phase I report, published in 2000, summarized interim results of the visibility, O_3, and atmospheric deposition subgroups of FLAG.

Monitoring lichen communities to assess management issues associated with air quality

McCune et al. (2006) summarized components of the NPS Inventory and Monitoring Program in the Sierra Nevada that focus on lichen monitoring. The principal objectives of Inventory and Monitoring efforts include providing scientifically valid data on status and trends of national park ecosystems. Existing data specific to Sierra Nevada ecosystems were synthesized as a first step toward assessing lichen communities as potential indicators of ecosystem change. Existing monitoring protocols applied by the Forest Service in the Sierra Nevada were summarized.

Lichens species can be divided into functional groups, based on their sensitivities to different stressors. For example, some species thrive in N-rich environments. It is likely that such nitrophilous lichens have increased in remote areas subjected to increased atmospheric N deposition (Joren and McCune 2005, 2006). Multivariate lichen community models (e.g., Joren and McCune 2005) can be developed to reflect the relative abundance of nitrophilous species, and therefore the relative contribution of N deposition. Similarly, N-fixing lichens are likely to decline in abundance in response to increased N deposition (McCune et al. 2006).

National Park Service Water Quality Inventory Protocols for Riverine Environments

The NPS Water Quality Inventory Protocols for Riverine Environments (Stednick and Gilbert 1998) outlines protocols for measuring stream discharge; sample collection, handling, and preservation; field-measured parameters; laboratory-measured parameters; QA/QC; electronic data acquisition; and data management and archiving. The purpose of this manual was to ensure that the collection of streamwater data in national parks is carried out using methods accepted by EPA and NPS, and so that the resulting data will be useful for resource management.

Aquatic Ecological Unit Inventory Technical Guide

The Forest Service develops resource inventory and monitoring technical guides to define national attributes and associated protocols governing resource inventory and monitoring needs of the Agency. As part of that effort, a draft technical guide for aquatic ecological and inventory efforts was prepared in October 2006 (Potyondy et al. 2006). It provides specific guidance for conducting an Aquatic Ecological Unit Inventory (AEUI) at the valley and river reach scales. The overall objective is to classify and map ecological types to a consistent standard throughout national forest lands. Some elements of this effort are also applicable to studies of ecological

effects of atmospheric deposition. Data standards and protocols are provided for obtaining basic physical, biological, and chemical information on stream systems suitable for addressing questions of status and trends.

<u>Lakewater Chemistry for Forest Service Pacific Southwest Region</u>

Berg and Grant (2006a, b) described the water quality and zooplankton data collection protocols for Project LAKES (Lake Alkalinity Evaluation in the Sierra Nevada), part of the Monitoring and Adaptive Management Plan of the Forest Service Pacific Southwest Region (USDA 2004). The major objective is to document lakewater status and change in response to air pollution. The focus is on water chemistry, transparency, and zooplankton community dynamics of low-ANC lakes in Class I wilderness areas during the snowmelt period. When the monitoring program is completely implemented, it will include about 20 lakes within the Class I and Class II wilderness areas in the Sierra Nevada.

3.7.3. Recommended Protocols Outline

The documents highlighted in the previous section may be helpful as the Forest Service begins the process of establishing a consistent set of field, laboratory, and analysis protocols for study of AQRVs in the Forest Service Air Program nationwide. We offer here some general recommendations that may help in the establishment of nationally-consistent protocols. We believe that the quality of aquatic and terrestrial sampling activities within the Air Program can be enhanced by focusing protocol development on such aspects as:

- training of field personnel
- efficient selection of variables for sampling and analysis
- consistency of field and laboratory protocols
- establishment of clear linkages between study objectives and sampling design
- documentation of methods
- rigorous QA/QC protocols
- efficient data management
- informed data analysis and interpretation

Development of standardized protocols for national implementation will be beneficial to the USDA Forest Service Air Program in its efforts to monitor and assess AQRVs. Although a

number of protocol compilations are highlighted in this report, the scope did not include development or recommendation of specific protocols in this report for field sampling or laboratory analysis. However, we provide in Table 3 a general outline of the kinds of items that should be considered for inclusion in a national AQRV monitoring and assessment protocol for the Air Program. Issues highlighted in Table 3 are important for protocols development for both terrestrial and aquatic receptors. Our objective in this report has not been to develop or recommend specific protocols. Rather, we explored the components of the process that will need to be included in a subsequent protocols development effort.

Table 3. Straw-person outline of AQRV monitoring protocols. (In part, modified from Oakley et al. 2003)

- 1.0 Protocol Narrative
    - 1.1 Background and objectives
        - 1.1.1 Resources sensitive to atmospheric deposition
        - 1.1.2 Rationale for selection of resources for characterization and monitoring
        - 1.1.3 Objectives and research questions
    - 1.2 Sampling design
        - 1.2.1 Rationale
        - 1.2.2 Site selection
        - 1.2.3 Sampling frequency and timing
        - 1.2.4 Replication
    - 1.3 Field methods
        - 1.3.1 Training requirements
        - 1.3.2 Preparations, equipment setup, and permitting
        - 1.3.3 Sequence of field activities
        - 1.3.4 Measurement procedures
        - 1.3.5 Sample collection procedures
        - 1.3.6 Post-collection sample processing
        - 1.3.7 End of season procedures
    - 1.4 Laboratory methods
        - 1.4.1 Instrumentation
        - 1.4.2 Lab protocols
        - 1.4.3 Replication
        - 1.4.4 Blanks, spikes, and standards
    - 1.5 Data development
        - 1.5.1 Metadata
        - 1.5.2 Database design
        - 1.5.3 Data entry, verification, editing
        - 1.5.4 Routine data summaries and internal consistency check
    - 1.6 Reporting
        - 1.6.1 Schedule
        - 1.6.2 Format with example tables and figures

1.6.2 Format with example tables and figures
1.6.3 Trends analysis
1.6.4 Data archive procedures
1.7 Personnel
1.7.1 Roles and responsibilities
1.7.2 Qualifications
1.7.3 Training
1.8 Operations requirements
1.8.1 Staffing, workload, and scheduling
1.8.2 Facility and equipment needs
1.8.3 Budget

2.0 List of Standard Operating Procedures
2.1 Pre-season setup
2.2 Training field personnel
2.3 Sampling site location (GPS, maps, compass, navigation)
2.4 Equipment use (vehicles, boats, snowmobiles, monitoring and measuring equipment
2.5 Plot establishment, marking, access protocols
2.6 On-site measurements
2.7 Sample collection
2.8 Data forms
2.9 Reporting
2.10 Equipment storage and field site close-up
2.11 Procedures for revising protocols and documenting changes

3.0 Data Management
3.1 Data management software
3.2 Data analysis or decision support tools
3.3 Example databases
3.4 Supplementary materials

4.0 Supplementary Materials

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4. SUMMARY

The USDA Forest Service collects and analyzes data on the sensitivity to, and the effects of, air pollution on aquatic and terrestrial ecosystems throughout the national forests nationwide. At the present time, there is no agreement regarding what sensitive ecosystem receptors should be studied, and there are no standard protocols to guide field sampling, laboratory analysis, or data analysis associated with such activities. This report summarizes the results of a scoping study to evaluate air quality related values (AQRVs) and associated existing field, laboratory,

and data analysis protocols to be used in characterizing the health and status of components of aquatic and terrestrial ecosystems that could be affected by atmospheric deposition of S, N, and toxics. The objective is to provide the foundation for developing a standard set of Forest Service AQRVs, sensitive receptors, indicators, and associated protocols to guide field studies on AQRVs nationwide.

Both chemical and biological sensitive receptors are assessed. Emphasis is placed primarily on acidification and eutrophication effects associated with deposition of S and N, and secondarily on effects associated with deposition of mercury (Hg), pesticides, or other toxic materials. We also provide a summary of a number of existing protocol documents which may be helpful in developing the Forest Service AQRV program.

A limited list of key variables does not exist with which to measure ecosystem condition, or ecosystem response to stress, such as from atmospheric deposition (i.e., acidification, eutrophication, toxicity). Ecosystems are highly complex, and simply cannot be represented by a small number of variables. Nevertheless, there are variables that have been shown to be, or that are expected to be (based on existing research), reflective of the general level of ecosystem harm that might be associated with atmospheric deposition. There are three ecological AQRVs on Forest Service land that are susceptible to air quality degradation: surface water, soil, and flora. There are a variety of sensitive receptors that have been shown to be important for each AQRV. Sensitive receptors for effects on surface water could include water chemistry, productivity, and the response of important life forms, including fish, zooplankton, benthic macroinvertebrates, and phytoplankton. Key sensitive receptors for assessing impacts on soil include soil chemistry and soil solution chemistry. Sensitive receptors for flora include macro-lichens and acid-sensitive vascular plant species.

We propose a set of consistent AQRVs and associated sensitive receptors that could be used by the Forest Service nationwide for evaluation of ecosystem sensitivity to, and effects from, atmospheric deposition. This is by no means an exhaustive list. Individual forests may wish to augment, or replace, some of the listed items in favor of other AQRV receptors that are especially important to a particular forest region or location, or for which that forest has specialized expertise. Nevertheless, the recommended AQRVs and sensitive receptors summarized here are broadly applicable and reflect a range of aquatic and terrestrial effects of atmospheric deposition. We also provide the foundation for development of standardized sampling and analysis protocols. The use of standardized protocols by the Air Program will

foster consistency across individual forests and maximize the Agency's ability to assess spatial and temporal trends in resource sensitivity and environmental effects. Use of consistent approaches in the collection and interpretation of environmental data will help efforts to understand cause/effect relationships among air pollution, biogeochemistry, natural resource sensitivity, and land management.

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7. APPENDICES

APPENDIX A
EXAMPLES OF RESEARCH ON THE EFFECTS OF ATMOSPHERIC DEPOSITION ON FISH

A.1. Effects on Brook Trout or Cutthroat Trout

Fish communities of acid-sensitive streams and lakes may contain a variety of species, but are often dominated by trout. Across the eastern United States, brook trout is often selected as an indicator of acidification effects on aquatic biota because it is native to many eastern streams and lakes and because residents place great recreational and aesthetic value on this species. It must be emphasized, however, that brook trout is a relatively acid-tolerant species. Many other fish species, including rainbow (*Oncorhynchus mykiss*) and brown (*Salmo trutta*) trout, as well as a variety of other fish species, are more acid-sensitive than brook trout. In many Appalachian Mountain streams that have been acidified by acidic deposition, brook trout is the last species to disappear; it is generally lost at pH near 5.0 (MacAvoy and Bulger 1995), which generally corresponds in these streams with ANC near zero (Sullivan et al. 2003).

In acid-sensitive streams and lakes in the western U.S., the focus is often mainly on native cutthroat trout. It is important to note, however, that many high-elevation western lakes and streams were historically fishless. The top predators in such aquatic ecosystems were often amphibians. Thus, even though cutthroat trout might be considered native to the region, they are not necessarily native to a particular lake or stream.

Effects on biota can be assessed as impacts on a particular sensitive or important species or as impacts on the diversity of fish or other potentially sensitive life form. For example, Bulger et al. (2000) developed ANC thresholds for brook trout in Virginia, which are presented in Table A1. These values were based on annual average streamwater chemistry, and therefore represent chronic exposure conditions. The likelihood of additional episodic stress is incorporated into the categories in the manner in which they are interpreted. For example, the episodically-acidic response category, which has chronic ANC in the range of 0 to 20 μeq/L, represents streams which are expected to acidify to ANC near or below zero during rainfall or snowmelt episodes. In such streams, sublethal and/or lethal effects on brook trout are possible (Bulger et al. 2000, Sullivan et al. 2003).

Streams with chronic ANC greater than about 50 μeq/L are generally considered suitable for brook trout in southeastern U.S. streams because they have a large enough buffering capacity

Table A1. Brook trout acidification response categories developed by Bulger et al. for streams in Virginia (2000).

Response Category	Chronic ANC Range (μeq/L)	Expected Response
Suitable	> 50	Reproducing brook trout expected if other habitat features are also suitable
Indeterminate	20 to 50	Brook trout response expected to be variable
Episodically acidic	0 to 20	Sub-lethal and/or lethal effects on brook trout are possible
Chronically acidic	< 0	Lethal effects on brook trout probable

that persistent acidification poses no threat to this species, and there is little likelihood of storm-induced acidic episodes lethal to brook trout. In such streams, reproducing brook trout populations are expected if the habitat is otherwise suitable (Bulger et al. 2000), although some streams may periodically experience episodic chemistry that affects species more sensitive than brook trout. Streams having annual average ANC from 20 to 50 μeq/L may or may not experience episodic acidification during storms that can be lethal to juvenile brook trout, as well as other fish. Streams that are designated as episodically acidic (chronic ANC from 0 to 20 μeq/L) are considered marginal for brook trout because acidic episodes are likely (Hyer et al. 1995), although the frequency and magnitude of episodes vary. Streams that are chronically acidic (chronic ANC less than 0 μeq/L) are not expected to support healthy brook trout populations (Bulger et al. 2000).

It is important to note, however, that acidity is not the only stress factor that influences the distribution of fish in acid-sensitive streams. Other habitat characteristics, including water temperature and stream channel morphology, can be important (Sullivan et al. 2003). In addition, it is likely that some trout populations have been affected by encroachment from other introduced species (c.f., Larson and Moore 1985).

A.1. Sublethal Effects

Sublethal effects, such as reduction in the condition factor (an index to describe the relationship between fish weight and length), have been shown for blacknose dace (*Rhinichthys atratulus*) near pH 6.0 (Dennis and Bulger 1995). This species is widely distributed in Appalachian Mountain streams and is relatively tolerant of low pH and ANC. Fish with higher condition factor are more robust than fish having low condition factor. Condition factor,

expressed as fish weight/length^3 multiplied by a scaling constant (Everhart and Youngs 1981), is interpreted as depletion of energy resources such as stored liver glycogen and body fat (Goede and Barton 1990). A positive relationship between condition factor and stream acid-base chemistry in Shenandoah National Park streams was found for the minimum pH recorded over the previous three years (corresponding with the approximate life span of blacknose dace). Observed differences in condition factor with decreasing pH were attributed to the likelihood that maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger 1999, Webb 2003, Sullivan et al. 2003).

Blacknose dace condition factor was compared by Bulger et al. (1999) in 11 streams spanning a range of pH/ANC conditions. Figure A1 shows the highly significant relationship between mean stream pH and blacknose dace condition factor. Note that the four populations represented on the left side of the figure all have mean pH values within or below the range of critical pH values, at which negative populations effects are likely for the species (Baker and Christensen 1991). That poor condition is related to population survival is suggested by the extirpation in 1997 of the blacknose dace population from the stream (Meadow Run) with the lowest pH and ANC (J. Atkinson, pers. comm.2002; Figure A1).

The results of the condition factor comparisons among the 11 streams indicated that the mean length-adjusted condition factor of fish from the stream with the lowest ANC was about 20% lower than that of the fish in best condition. Comparisons with the work of Schofield and Driscoll (1987) and Kretser et al. (1989) suggest that pH in the low-pH Shenandoah National Park streams is also near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan et al. 2003).

Smaller blacknose dace body size could result from direct toxicity (e.g., elevated energy use to compensate for sublethal ionoregulatory stress) or from reduced access to food or lower food quality (Baker et al. 1990c). Primary productivity is low in headwater streams and lower still in softwater headwaters, which are more likely to be acidified. Production of invertebrates is likely to be low in such streams as well (Wallace et al. 1992). Thus, lower food availability cannot be ruled out as a potential contributor to lowered condition in Shenandoah National Park blacknose dace populations. Nevertheless, reduced growth rates have been attributed to acid stress in a number of other fish species, including Atlantic salmon, chinook salmon, lake trout, rainbow trout, brook trout, brown trout, and Arctic char. Furthermore, the blacknose dace

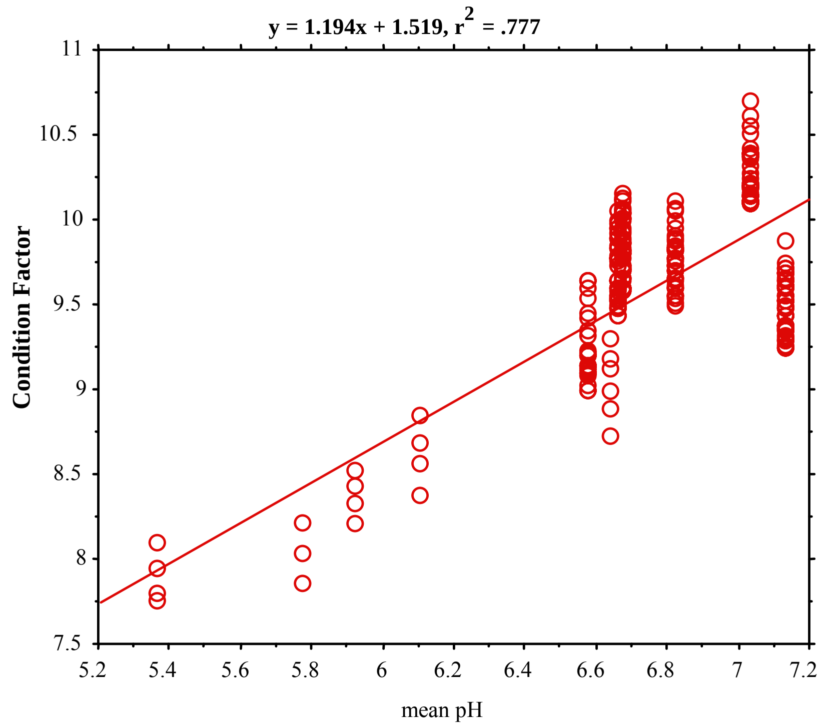


Figure A1. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n=442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The regression analysis showed a highly significant relationship ($p \leq 0.0001$) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams. (Source: Sullivan et al. 2003)

population in poorest condition in Shenandoah National Park occurred in a stream with mean pH below the minimum recorded for blacknose dace populations in Vermont, New Hampshire, Maine and New York (Baker et al. 1990b). The four blacknose dace populations in poorest condition in Shenandoah National Park occurred in streams at or below the critical pH for the species, where adverse effects due to acidification are likely to be detectable at the population level (Baker et al 1990b). Consequently, acid stress is probably at least partly responsible for the lower condition of blacknose dace populations in Shenandoah National Park, though lower food availability, either resulting from the nature of softwater streams or exacerbated by acidification, cannot be ruled out (Sullivan et al. 2003).

Chronic sublethal stress reduces growth in fish, as well as reproductive success (Wedemeyer et al. 1990). Chronic sublethal stress caused by pH levels below about 6.0 may have serious effects on a variety of wild fish populations. There is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total

energy budget and are unavailable for other functions, such as growth (Schreck 1981, 1982). The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish 1969, Bulger 1986). Because of the steep gradient in Na^+ and Cl^- concentrations between fish blood and freshwater, there is constant diffusional loss of these ions, which must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-); and Al elevates losses of Na^+ and Cl^- above the levels due to acid stress alone (Wood 1989).

The use of condition factor has been developed and applied mainly for blacknose dace, a widely distributed fish species. However, the concept is likely applicable to other species as well. We expect that fish condition factor would be a useful metric for many species across the nation. It may be especially useful in aquatic ecosystems that are only marginally affected by acidification. Changes in fish condition factor may be manifested before other changes become apparent in such metrics as brook trout presence or fish species richness.

A.2. Effects on Fish Species Richness

A direct outcome of fish population loss as a result of acidification is a decline in species richness (the total number of species in a lake or stream). This appears to be a highly predictable outcome of regional acidification, although the pattern and rate of species loss varies from region to region. Baker et al. (1990c) discussed 10 selected studies which documented this phenomenon, with sample sizes ranging from 12 to nearly 3,000 lakes or streams analyzed per study.

Effects of surface water acidification on fish species richness have been recently studied in some detail in the St. Marys River and Shenandoah National Park in Virginia, and in the Adirondack Mountains in New York. At all three locations, fish species richness has been found to be closely associated with surface water acid-base chemistry. The St. Marys River studies have examined changes in one stream over time. The Shenandoah National Park and Adirondack Park studies have examined differences across streams or lakes at a given time (space-for-time substitution analysis).

Bugas et al. (1999) conducted electrofishing in the St. Marys River in 1976, and every two years from 1986 through 1998. Systemic streamwater acidification occurred during the study period. Sampling occurred at six sites between the wilderness area boundary at the downstream end and the headwaters over a distance of about 8 km. The number of fish species

in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter) are typically the only fish species present in streams having similar levels of acidity in Shenandoah National Park, which is also located in Virginia (Bulger et al. 1999, Webb 2003). Bugas et al. (1999) reported that successful brook trout reproduction in the St. Marys River occurred only one year out of four during the period 1995 through 1998. Eight of the fish species recorded in one or more early years have not been observed in more recent years. Several, including blacknose dace, rainbow trout, and torrent sucker, showed a pattern of being progressively restricted over time to lower river reaches, which generally have higher ANC.

Rosyside dace (*Clinostomus funduloides*) and torrent sucker (*Thoburnia rhothocea*) were last present in 1996; Johnny darter (*Etheostoma nigrum*) and brown trout were last present in 1994; rainbow trout and longnose dace (*Rhinichthys cataractae*) were last present in 1992; bluehead chub (*Nocomis leptocephalus*) and smallmouth bass (*Micropterus dolomieui*) were last present in 1990 and 1988, respectively; white sucker (*Catastomus commersoni*) and central stoneroller (*Campostoma anomalum*) were last present in 1986. Of the four remaining species, three (blacknose dace, fantail darter [*Etheostoma flabellare*]), and mottled sculpin [*Cottus bairdi*]) have declined in density and/or biomass; the fourth remaining species is brook trout, the region's most acid tolerant species; this population has fluctuated, and reproductive success has been sporadic. Blacknose dace, once abundant throughout the river, remain only at the lowest sampling station, which has the highest pH, and at such low numbers (five individuals in 1998) that they might be strays from downstream. For some of the species (smallmouth bass, white sucker, the three trout, and blacknose dace) the critical pH is known, and their decline and/or extirpation, given the pH of the river, is not surprising (Sullivan et al. 2003).

Although there are known differences in acid sensitivity among fish species, experimentally-determined acid sensitivities are available for only a minority of freshwater fish species. Baker and Christensen (1991) reported critical pH values for 25 species of fish. They defined critical pH as the threshold for significant adverse effects on fish populations. The range of response within species depends on differences in sensitivity among life stages, and on different exposure concentrations of calcium (Ca^{2+}) and Al. Relative sensitivities can be suggested by regional surveys as well, although interpretation of such data is complicated by factors that correlate with elevation. Such factors, including habitat complexity and refugia from high-flow conditions, often vary with elevation in parallel with acid sensitivity. It is the

difference in acid tolerance among species that produces a gradual decline in species richness as acidification progresses, with the most sensitive species lost first (Sullivan et al. 2003).

Relatively less is known about changes in fish biomass, density and condition (robustness of individual fish) which occur in the course of acidification. Such changes result in part from both indirect and direct interactions within the fish community. Loss of sensitive individuals within species (such as early life stages) may reduce competition for food among the survivors, resulting in better growth rates, survival, or condition. Similarly, competitive release (increase in growth or abundance subsequent to removal of a competitor) may result from the loss of a sensitive species, with positive effects on the density, growth, or survival of competitor population(s) of other species (Baker et al. 1990b). In some cases where acidification continued, transient positive effects on size of surviving fish were shortly followed by extirpation (Bulger et al. 1993).

The FISH Project quantified the effects of acidification on streams within Shenandoah National Park (Bulger et al. 1999). This project examined fish response on multiple levels, including condition factor for blacknose dace, increased mortality of brook trout, and fish species richness. All three indicators of biological response were closely correlated with stream acid-base chemistry. In southern Appalachian streams, local species richness of the various animal life forms depends on thermal regime, water chemistry, patterns of discharge, plus substrate type and geomorphology (Wallace et al. 1992). Acidity is only one factor among many determining species composition of Appalachian streams. This is an important consideration when evaluating the biological implications of changes in water chemistry (Sullivan et al. 2003).

Bulger et al. (1999) demonstrated a strong relationship between stream ANC and the number of fish species found in each stream (Figure A2). Presumably, streamwater acidification reduced species richness by eliminating the more sensitive species as pH and ANC declined (Baker and Christiansen 1991). In addition, however, it is likely that watershed area played a role in this observed relationship. Smaller watershed areas are often associated with fewer fish species.

There are clear patterns in species distribution from headwater streams in the uplands to larger rivers in the lowlands. These patterns can also be seen in community comparisons among reaches at different elevations. The clearest pattern is that species richness increases in a downstream direction. There is typically a rather small number of species that can tolerate the

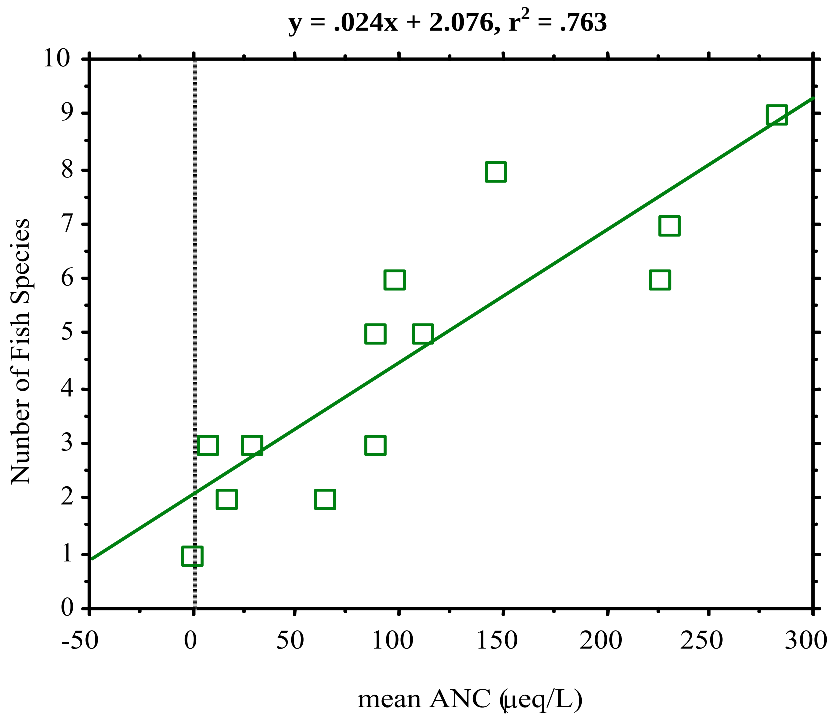


Figure A2. Number of fish species among 13 streams in SHEN. Values of ANC are means based on quarterly measurements, 1987-94. The regression analysis showed a highly significant relationship ($p \leq 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently < 75 µeq/L had three or fewer species. (Source: Bulger et al. 1999, Sullivan et al. 2003)

high current velocities and low pH often found in upstream reaches. In the highest headwaters, fish are absent and are replaced by salamanders (Sullivan et al. 2003).

In most river systems in acid-sensitive regions of the U.S., the highest-elevation streams are the smallest, coldest, highest-gradient (steepest) streams, with fewest species of fish. There is a general pattern of increasing fish species richness and abundance from higher to lower elevation, probably resulting in part from a greater variety of habitat types (including spawning and nursery areas) and food sources in downstream reaches. Thus, many headwater streams with lower pH might be expected to have fewer fish species than lower elevation streams, regardless of pH (Sullivan et al. 2003).

The effects of acidification interact with other habitat characteristics to determine the species and biological communities that will occur in a given stream reach. The effects of streamwater acid-base chemistry on aquatic biota were summarized by Baker et al. (1990c) and

Bulger et al. (1999). Suitable streamwater acid-base chemistry is a necessary, but not necessarily sufficient, prerequisite for supporting brook trout, or any other species or biological community.

Bulger et al. (1999) analyzed the relationship between number of fish species in Shenandoah National Park streams and the minimum recorded ANC for each stream (Figure A2). The number of fish species decreased with decreasing minimum ANC, from 9 species at ANC of about 160 μeq/L to 1 to 3 species at ANC near zero. The best fit regression line suggested, on average, a loss of one species for every 21 μeq/L decline in minimum ANC.

Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress. An additional causal factor is likely the increase in the number of available aquatic niches as you move from upstream locations (which are often low in pH and ANC in this region) to downstream locations (which are seldom low in pH and ANC; Sullivan et al. 2003). The relative importance of this latter factor, compared with the importance of acid stress, in determining this relationship, is not known. The minimum recorded ANC accounted for 82% of the variance in fish species richness. However, the analysis included both very small headwater streams and larger rivers, some of which contained many species of fish. Those containing more than five species of fish generally are not small headwater streams (Table A2). Small headwater streams contain one species (brook trout) or in some cases a few species, and as you move higher in the stream system, eventually contain no fish species at all.

Median streamwater ANC values and watershed areas are shown in Table A2 for the 13 streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species richness. These study streams include several larger streams (North Fork Thornton River, Piney River, Rose River, Staunton River, Hazel River). All of the "rivers" have watersheds larger than 4 mi^2 and ANC higher than 75 μeq/L. In contrast, the majority (but not all) of the "runs" (or streams) have watershed area smaller than 4 mi^2 and ANC less than 20 μeq/L. All of the streams that have watershed areas smaller than 4 mi^2 have 3 or fewer known species of fish present. The ANC of the smaller streams is determined largely by the underlying geology. All of the streams having larger watersheds (> 4 mi^2) have 3 or more known fish species; 7 of 8 have 5 or more species; and the average number of fish species is 6 (Sullivan et al. 2003). There is no clear distinction between river and run, but it is clear that as small streams in this region combine and flow into larger streams and eventually to rivers, two things happen: acid-sensitivity generally declines, and habitat generally becomes suitable for additional fish species.

Table A2. Median streamwater ANC and watershed area of streams used by Bulger et al. (1999) to evaluate the relationship between ANC and fish species richness. (Source: Sullivan et al. 2003)

Site ID	Watershed Area (mi^2)	Median ANC (µeq/L)	Number of Fish Species[a]
Smaller Watersheds (< 4 mi^2)			
North Fork Dry Run	0.9	48.7	2
Deep Run	1.4	0.3	N.D.[b]
White Oak Run	1.9	16.2	3
Two Mile Run	2.1	10.0	2
Meadow Run	3.4	-3.1	1
Brokenback Run	3.9	74.4	3
Larger Watersheds (4-10 mi^2)			
Staunton River	4.1	76.8	5
Piney River	4.8	191.9	7
Paine Run	4.9	3.7	3
Hazel River	5.1	86.8	6
White Oak Canyon	5.4	119.3	7
N. Fork Thornton River	7.3	249.1	9
Jeremy's Run	8.5	158.5	6
Rose River	9.1	133.6	8

[a] Data regarding number of fish species were provided by A. Bulger, University of Virginia.
[b] Data were not available regarding the number of fish species in Deep Run.

Watershed area can be important in this context because smaller watersheds generally contain smaller streams having less diversity of habitat, more pronounced impacts on fish from high flow periods, and often lower food availability. Such issues interact with other stresses, including acidification, to determine habitat suitability.

Sullivan et al. (2006) developed a relationship between fish species richness and ANC class for Adirondack lakes (Figure A3). Fish species richness observations were fit to a logistic relationship by a non-linear regression analysis. The relationship for species richness as a function of ANC was:

$$Fish\ Species\ Richness = 0.18 + \left[\frac{5.7}{1 + \left(\frac{ANC}{28} \right)^{-1.63}} \right] \quad (r^2 = 0.9)$$

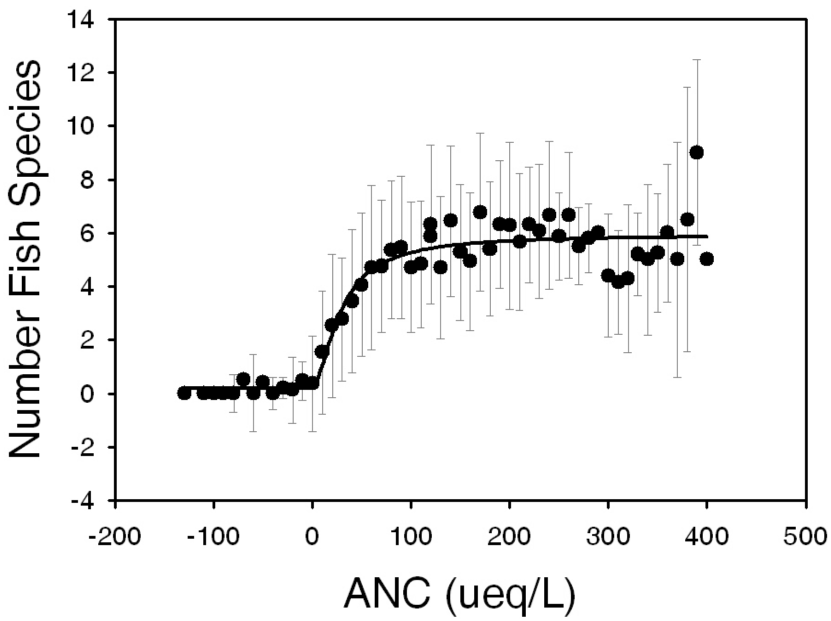


Figure A3. Fish species richness of Adirondack lakes as a function of ANC. The values shown represent the mean (filled circles) and standard deviation (bars) of 10 µeq/L ANC classes. Also shown as a solid line is the application of the logistic model. (Source: Sullivan et al. 2006)

where ANC is in µeq/L. Under chronically acidic conditions (summer index or annual average ANC< 0 µeq/L), Adirondack lakes are generally fishless. There was a marked increase in mean species richness with increases in ANC up to near values of 50 to 100 µeq/L. The asymptote for the fish species equation was 5.7 species.

This analysis suggests that there could be loss of fish species with decreases in ANC starting at values around 100 µeq/L. It does not account, however, for the possibility that lakes having higher ANC often tend to be larger, and therefore support more fish species due to increased habitat diversity and complexity.

APPENDIX B
EXAMPLE STUDIES ILLUSTRATING ACIDIFICATION EFFECTS ON STREAM MACROINVERTEBRATES

Benthic macroinvertebrates have been monitored in Shenandoah National Park streams since 1986 as part of the Long-Term Ecological Monitoring System (LTEMS). Moeykens and Voshell (2002) examined streamwater chemistry of 89 sites (28 low-ANC sites and 61 higher-ANC sites) for which macroinvertebrate data were available. They compared their results for streams in the park with similar analyses for 45 sites (13 low-ANC sites and 32 higher-ANC sites) elsewhere in the Blue Ridge ecoregion of Virginia. Moeykens and Voshell (2002) concluded that the higher-ANC streams had “superior ecological condition,” but that acidification of streamwater causes the only conspicuous degradation of macroinvertebrate communities in some low-ANC streams. Other disturbances, such as fire and flood, did not appear to have had noticeable long-term effects on the streams. Acidified streams host fewer invertebrate taxa and fewer functional groups than streams with higher pH and ANC. Similar findings were reported earlier for Shenandoah National Park streams by Feldman and Connor (1992).

Quantitative relationships between invertebrate communities and streamwater quality in SHEN streams were analyzed by Sullivan et al. (2003). Quarterly water quality data for 14 streams (1988-2001) were compared with LTEMS benthic invertebrate data.

There are 9 orders and 79 families of aquatic insects present in the Shenandoah National Park LTEMS samples. Not all families are present in each stream. The total number of insect families found in a given stream during the sampling period varied from 21 to 56. Of the nine orders of aquatic insects found in SHEN streams, there were three which were most abundant both in terms of frequency of occurrence in samples and total numbers of individuals collected: Ephemeroptera (mayflies); Plecoptera (stoneflies); and Trichoptera (caddisflies). The use of these three orders as indicators of acidification response in streams is well established. A combined metric based on all three families, the Ephemeroptera-Plecoptera-Trichoptera (EPT) index, is one measure of stream macroinvertebrate community integrity. This is the total number of families in the three insect orders present in a collection. These orders contain families of varying acid sensitivity so the index value (the number of families) is lower at acidified sites (c.f., SAMAB 1996). In general, mayflies (Ephemeroptera) are most sensitive to acidity, and

stoneflies (Plecoptera) are least sensitive. Caddisflies (Trichoptera) are intermediate (Peterson and Van Eeckhaute 1992).

Positive relationships were observed between mean and minimum streamwater ANC and the number of families in the orders Ephemeroptera and Plecoptera, but less so for Tricoptera (Figure B1). The total numbers of individuals in the orders Ephemeroptera and Trichoptera were also related to the mean and minimum ANC values of the 14 streams (Figure B2). The EPT index provides a single measure of all three orders and was, as expected, also related to mean and minimum streamwater ANC (Figure B3). These data can be used to estimate the increase in the number of individuals of the orders Ephemeroptera or Tricoptera, or the number of families of all three orders, that might be expected to occur in response to a given increase or decrease in stream ANC (Sullivan et al. 2003).

As described by Kauffman et al. (1999), the record for St. Marys River provides a unique opportunity to compare reliable macroinvertebrate data on an acidified stream over a 60-year time span. Surber (1951) collected the earliest benthic data for St. Marys River. Starting in August of 1935, and continuing for two years, he collected 20 samples per month from the river's main stem. Subsequent data were collected by the Virginia Department of Game and Inland Fisheries (VDGIF) in 1976 and then biennially beginning in 1986 (Kauffman et al. 1999) using methods comparable to those used for the 1930s collections. The VDGIF data were collected at six evenly spaced locations extending the length of the main stem above the Wilderness boundary. The later collections were made in June, and only June data are used in the following comparisons, which were reported by Sullivan et al. (2003). The total abundance of mayfly larva in the St. Marys River has dramatically decreased over the 60-year period, and two of the mayfly genera, Paraleptophlebia and Epeorus, were last collected in 1976. Mayflies are known to decline in species abundance and richness with increasing acidity (Peterson and Van Eeckhaute 1992, Kobuszewski and Perry 1993). The total abundance of caddisfly (Trichoptera) larva also declined dramatically over the 60-year period of record. Baker et al. (1990b) indicated that caddisflies exhibit a wide range of response to acidity, with some species affected by even moderate acidity levels. The total abundance of the larva of the stonefly (Plecoptera) genera Leuctra/Alloperla has dramatically increased over the 60-year period. Increased abundance of these stoneflies in acidified waters has been well documented (Kimmel and Murphy 1985).

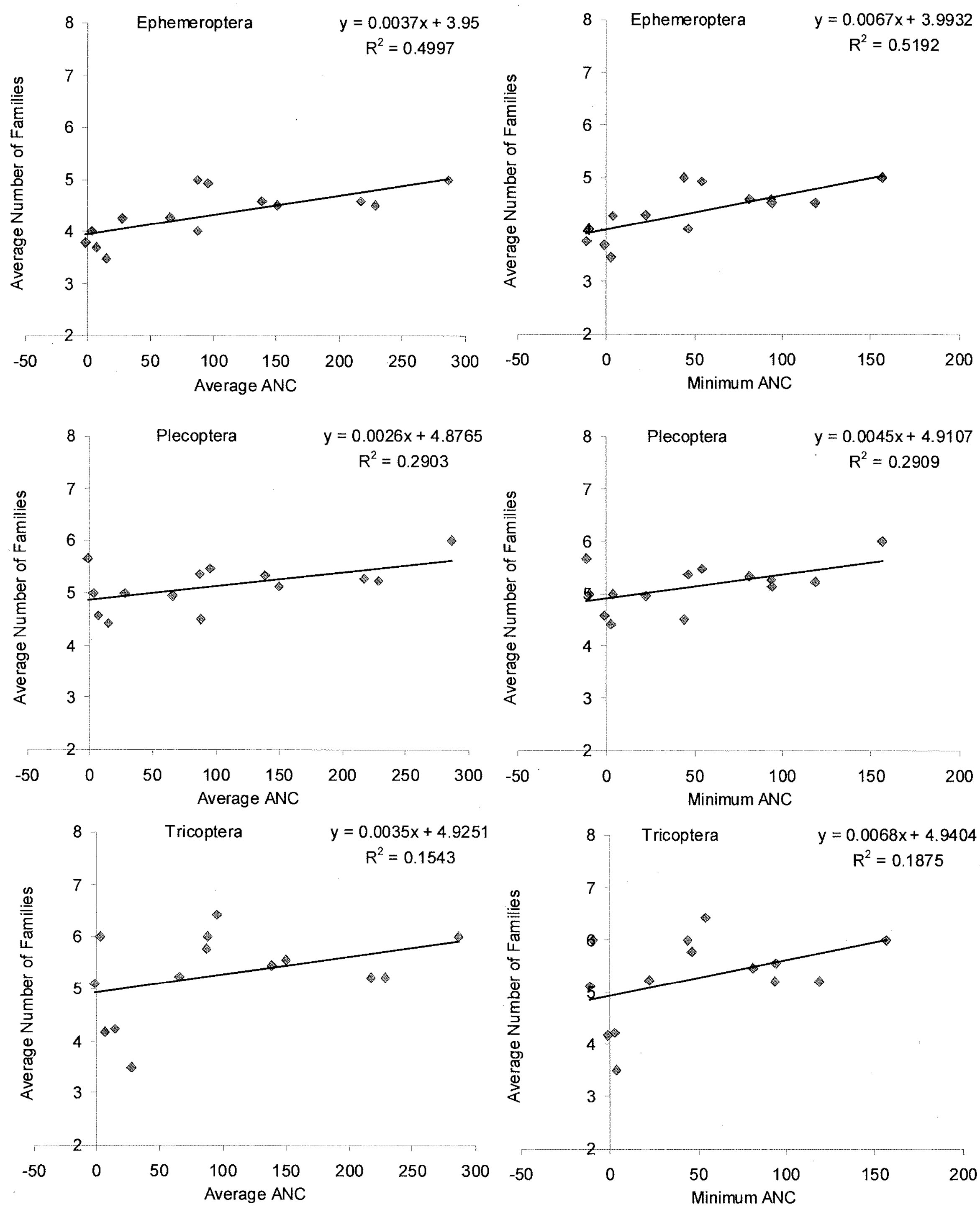


Figure B1. Average number of families of aquatic insects in a sample for each of 14 streams in SHEN versus the mean (left) or minimum (right) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. Results are presented for the orders Ephemeroptera (top), Plecoptera (center), and Tricoptera (bottom). The regression relationship and correlation are given on each diagram. (Source: Sullivan et al. 2003)

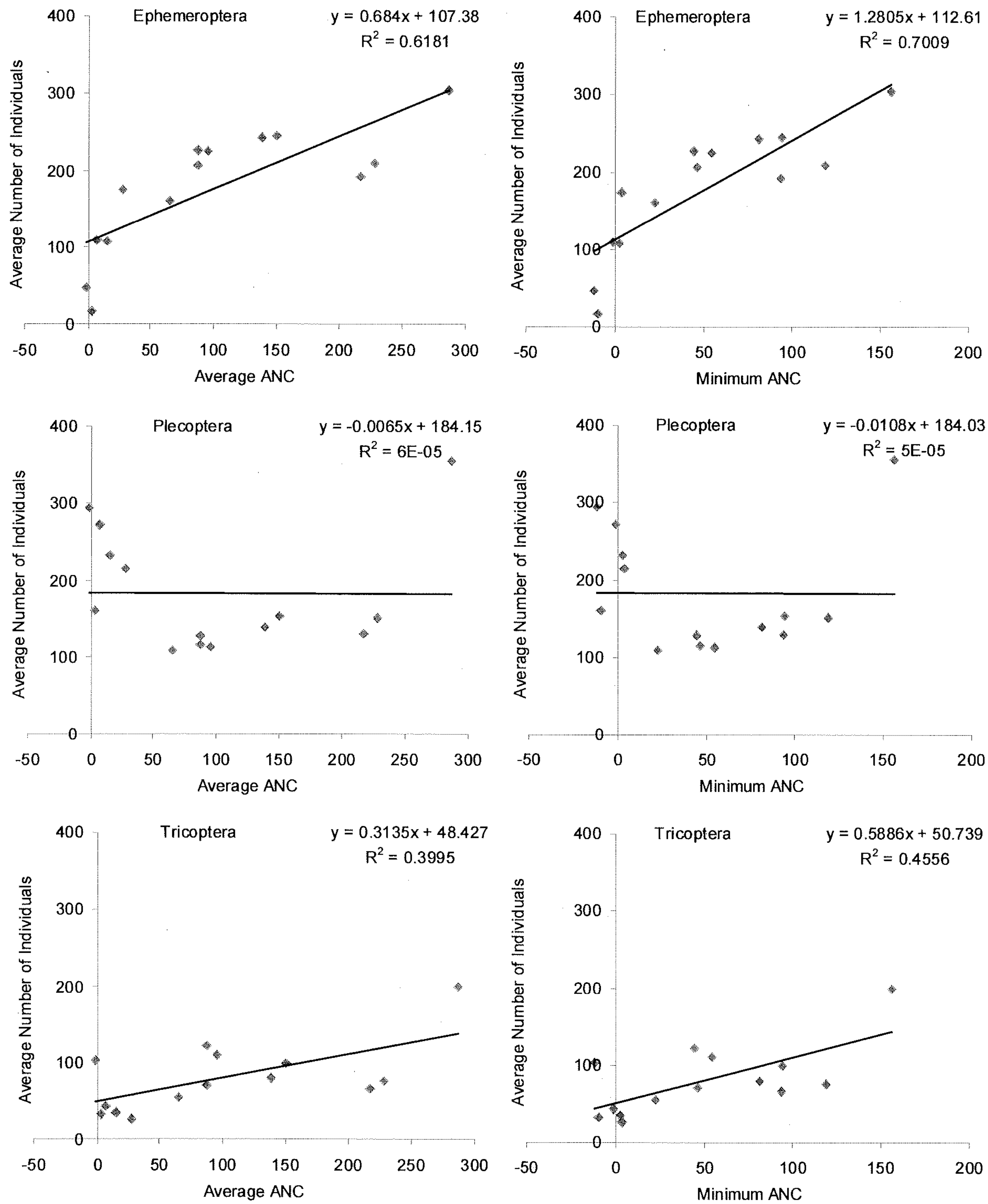
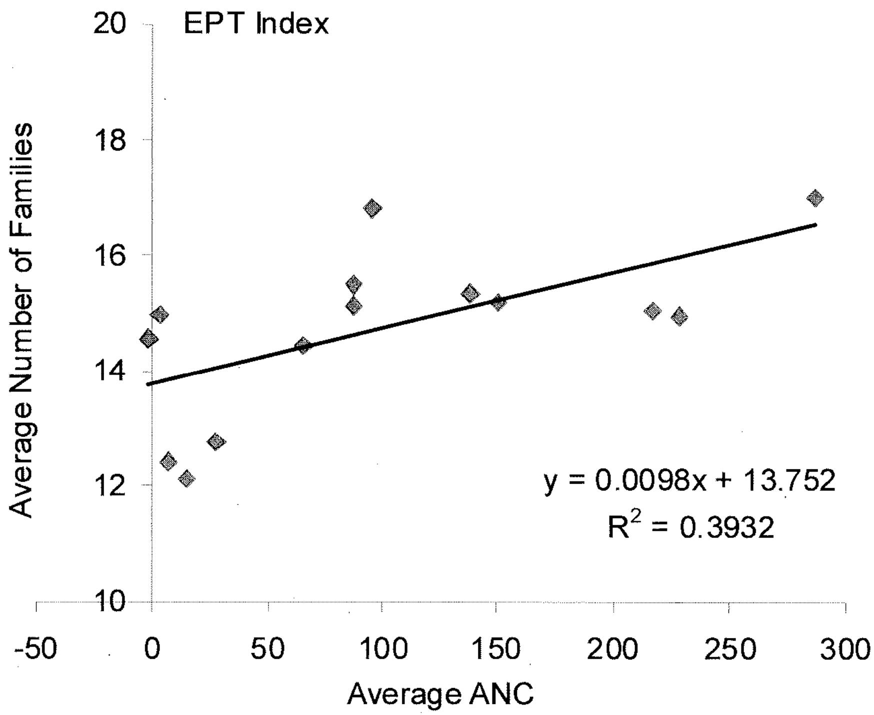


Figure B2. Average total number of individuals of aquatic insects in a sample for each of 14 streams in SHEN versus the mean (left) or minimum (right) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. Results are presented for the orders Ephemeroptera (top), Plecoptera (center), and Tricoptera (bottom). The regression relationship and correlation are given on each diagram. (Source: Sullivan et al. 2003)



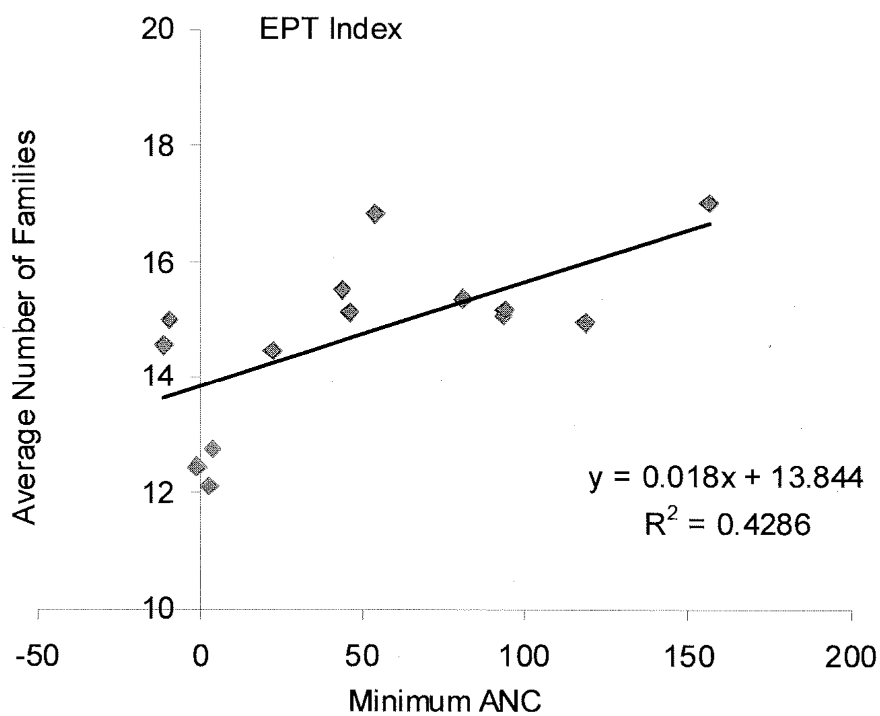


Figure B3. Average EPT index in a sample for each of 14 streams in SHEN versus the mean (top) or minimum (bottom) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. The regression relationship and correlation are given on each diagram. (Source: Sullivan et al. 2003)

Another insect family that has prospered in St. Marys River is the midge (Chironomidae), whose larval population has increased tenfold since the 1930s collections. Increased midge abundance in acidified waters has also been well documented (Kimmel and Murphy 1985, Baker et al. 1990b).

The St. Marys River watershed is underlain by siliceous bedrock and had measured ANC in the late 1990s generally between about –5 and 15 μeq/L, with a 10-year median value of 4 μeq/L (Webb 2003). In 1936 and 1937, the numbers of benthic invertebrate taxa collected were 32 and 29, respectively. The number of taxa declined to 23 in 1976. During the period 1986 through 1998, the average number of benthic invertebrate taxa collected was down to 17, varying from 13 to 22 in a given year (Webb 2003). Acid-sensitive mayflies and caddisflies decreased in abundance, and some more acid-tolerant invertebrate taxa increased in abundance (Webb 2003), probably due to reduced competition.

Effects of acidification on aquatic invertebrates were investigated in streams within GRSMNP by Rosemond et al. (1992). They determined patterns in benthic invertebrate community structure in four streams, with baseflow pH ranging from 4.5 to 6.8. A number of studies and analyses were conducted at these stream locations, including identification of sensitive species, toxicity (*in situ* transplant and exposure) tests, and assessment of differences in species richness, diversity, and density.

Rosemond et al. (1992) transplanted and placed into flow-through chambers three species of acid-sensitive mayfly between high and low pH streams. A transplant of *Drunella conestee* from pH 6.4 to 5.0 did not show a statistically-significant increase in mortality. In contrast, transplants of *Stenonema* sp. and *Epeorus pleuralis* from pH 6.4 to 5.0 showed 100% mortality of *Epeorus pleuralis* (20% for control) and 18% mortality for *Stenonema* sp. (0% for control) after 8 and 4 day exposures, respectively. Similarly, Mackay and Kersey (1985) found that *Stenonema* sp. was restricted to pH greater than 5.3 in streams in Ontario, and similar results have been found for *Epeorus* in the northeastern United States (Hall et al. 1980).

Rosemond et al. (1992) found increasing species richness of Ephemeroptera (Richness = 2.09 x pH – 8.5; r^2=0.96; $P < 0.05$) and Trichoptera (Richness = 1.52 x pH – 4.1; r^2=0.96; $P < 0.05$) with increasing pH, but no significant relationship with pH for Plecoptera. In both the Ephemeroptera and Trichoptera evaluations, there was found about 1.5 to 2 additional insect species of a given order for a rise in pH of 1 pH unit. Mayflies of the family Ephemerellidae

appeared to be especially acid-sensitive, and are often restricted to streams having pH above about 5.0 (Fiance 1978, Harriman and Morrison 1982, Rosemond et al. 1992).

APPENDIX C

EVIDENCE FOR EFFECTS OF ATMOSPHERIC DEPOSITION ON SPRUCE-FIR FORESTS IN THE SOUTHERN APPALACHIAN MOUNTAINS

(from Sullivan et al. 2002)

A number of studies suggest that acidic deposition has impacted high-elevation spruce-fir forests in the southern Appalachian Mountains (SA). These ecosystems are geographically limited within the region, occurring primarily at elevations above about 1400 m in southwestern Virginia, eastern Tennessee, and western North Carolina. Much of the research conducted to date has focused on Great Smoky Mountains National Park (which contains 74% of the spruce-fir forests in the region), White Top Mountain, VA, and Mt. Mitchell, NC (Eagar et al. 1996). This ecosystem experiences high precipitation (near 200 cm per year), high humidity, and frequent cloud cover. Atmospheric deposition of S and N can be very high and can include substantial cloud deposition (Mohner 1992).

Soil processes and nutrient cycling have been intensively studied at a number of sites in the SA, including three spruce-fir sites. The Integrated Forest Study (IFS) included five sites in or near Great Smoky Mountains National Park, two of which were red spruce (Tower and Becking sites). The SFRC and Tennessee Valley Authority sponsored research on a red spruce stand on White Top Mountain, and the Spruce-Fir Research Cooperative also sponsored research on spruce forest soils in the Black Mountains, NC. High-elevation areas in the SA are often dominated by sandstone and other unreactive bedrock. Base cation production via weathering is limited (Elwood et al. 1991). Soils of spruce-fir forests in the SA region tend to have thick organic horizons, high organic matter content in the mineral soils, and low pH (Joslin et al. 1992). Because of the largely unreactive bedrock, base-poor litter and organic acid anions produced by the conifers, high precipitation, and high base cation leaching rates in these high-elevation forests, soil base saturation tends to be below 10% and the soil cation exchange complex is generally dominated by aluminum (Johnson and Fernandez 1992, Joslin et al. 1992).

Spruce-fir forests in the SA, especially those at high elevation, receive high atmospheric deposition of N and show a number of signs of approaching N saturation, including:

- high concentrations of NO_3^- in soil solution and streamwater throughout the year,
- NO_3^- leaching losses that sometimes approach atmospheric inputs (Nodvin et al. 1995, Van Miegroet et al. 2001),

- N mineralization in excess of N-uptake requirements of plants,
- lack of tree growth response to N fertilization (Johnson et al. 1991b, Joslin and Wolfe 1992, Eagar et al. 1996), and
- Sensitivity of red spruce to moderate levels of soil solution aluminum and moderately low Ca/Al ratios (Raynal et al. 1989, Cronan and Grigal 1995).

Areas that have experienced a decline in tree growth or increased mortality (for example from balsam wooly adelgid infestation) are expected to be particularly susceptible to accelerated NO_3^- leaching and associated adverse impacts of N saturation on forest health. However, the dense reoccupation of some of these sites with rapidly-growing Fraser fir regeneration, which is capable of taking up considerable N and incorporating it in new growth, may minimize this adverse impact (Hinesley et al. 2000, Smith and Nicholas 2000).

Radial growth of spruce trees has decreased at high elevation in the SA, but this effect has apparently been limited to elevations above 5000 ft (1520 m). The decline began about 1960, and could not be attributed to unusual climate or stand competition (McLaughlin et al. 1987, Cook and Zelaker 1992). Wood chemistry has changed in parallel with growth. An increase in aluminum relative to calcium began to occur in wood produced by high-elevation red spruce trees in Great Smoky Mountains National Park in about the 1950s (Bondietti et al. 1989).

Sapling trees growing in the same area experienced a reduction in photosynthesis relative to respiration (P:R; reflecting decreased carbon metabolism efficiency) in association with increased foliar aluminum, decreased foliar calcium, and decreased Ca:Al ratio in soil solution (McLaughlin et al. 1993). In fact, soil solution chemistry data collected at high elevation sites in the park have frequently shown aluminum concentrations sufficiently high as to interfere with calcium uptake by trees.

Decreased foliar calcium has been attributed to exposure to acidic cloudwater (Joslin et al. 1988, McLaughlin et al. 1993, Thornton et al. 1994, Eagar et al. 1996). At least two studies have shown that acidic cloudwater affects membrane-associated CA in leaf cells, leading to consistent reductions in foliar cold tolerance (Jiang and Jagels 1999, Schaberg et al. 2000). Greenhouse studies have also shown that red spruce tree seedling P:R ratios were reduced by acidic exposure (McLaughlin et al. 1993).

Joslin et al. (1992) further documented reduced growth of roots into deeper mineral soils, as compared with upper organic soils which tend to have more favorable aluminum chemistry. It is also clear that changes in calcium availability are important for tree growth at these high-

elevation sites. This evidence has come from greenhouse and field fertilization studies (Van Miegroet et al. 1993, Joslin and Wolfe 1994). Soil aluminum treatments have also been repeatedly demonstrated to reduce foliar concentrations of calcium, magnesium, and other nutrients, as well as reducing growth and net photosynthesis (Raynal et al 1989, Schaberg et al. 2000). McNulty et al. (1996) demonstrated that N additions of 16 to 31 kg N/ha/yr to sites receiving low N atmospheric deposition in Vermont (5 kg N/ha/yr) resulted in (1) reduced foliar Ca:Al ratios in spruce, fir and birch trees and (2) increased rates of decline and reduced basal area growth. In contrast, Jacobson et al. (2000) found no impact 13 years later on plant nutrient concentrations of 20 years of N additions (at 24 to 120 kg N/ha/yr) to Norway spruce stands in Sweden.

Despite evidence suggesting impacts of acidic deposition on red spruce health, widespread decline of red spruce in the SA has not been documented (Cook and Zadaker 1992, LeBlanc et al. 1992). Decreased crown condition of red spruce in the 1980s was noted in several areas (Peart et al. 1992, Bruck et al. 1989), but long-term mortality rates have appeared stable (Nicholas 1992, Eagar et al. 1996, Smith and Nicholas 1999). Pauley et al. (1996) also found no unusual mortality or health symptoms in red spruce in the Great Smoky Mountains. Further, in places where red spruce mortality has occurred in the Northeast, red spruce appears to be maintaining its composition fraction in the recovering forest, though balsam fir and birches are growing faster than red spruce (Battles and Fahey 2000). It is also possible that recent observed decreases in the growth rate of high-elevation southern red spruce may be part of a long-term, climate-induced pattern of fluctuation, and may not be unusual compared with data from the past 200 years (LeBlanc et al. 1992, Reams et al. 1993, Eagar et al. 1996). In addition to acidic deposition, other important factors contributing to red spruce growth and health might include drought and increased exposure to wind and ice storms subsequent to the death of neighboring fir trees from balsam wooly adelgid infestation (Zedaker et al. 1988, Nicholas et al. 1992, Eagar et al. 1996). Nevertheless, there is considerable evidence that spruce growth and health have declined at high elevation in the SA, and that acidic deposition has played a role in such effects.

The evidence for adverse effects of acidic deposition on Fraser fir in the SA is less compelling. Eagar et al. (1996) concluded that Fraser fir populations were deteriorating throughout the region. There is evidence from tree ring studies that Fraser fir in Great Smoky Mountains National Park began a growth decline in about 1960 (McLaughlin et al. 1984). Inadequate calcium supply could play a role in the resistance of Fraser fir to adelgid infestation,

but no scientific evidence has been presented to support this relationship (c.f., Manion 1981). While Fraser fir seedlings are rapidly re-occupying many areas of adult fir mortality, there is considerable evidence that the shortage of reproducing Fraser fir adults, due to adelgid-caused mortality, will eventually lead to progressive decreases in replacement (Smith and Nicholas 2000). In contrast to red spruce, studies on Fraser fir Christmas trees have demonstrated the ability of the species to take up and effectively utilize N at high rates of application (up to 170 kg N/ha/yr; Hinesley et al. 2000).